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PHOTOMETRIC TITRATIONS

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Summary—Within the last few years, photometric titration has become an increasingly important analytical method. The principles of the method are discussed and sources of error briefly mentioned. A comprehensive review of recent applications of the technique is given.

IN this paper, an outline is given of the analytical application of photometric titrations, and material published in the period 1954 to mid-1957 is reviewed. Reference is also made to papers appearing up to the end of 1957 in the more readily available analytical journals. Papers published before the beginning of 1954 have been adequately reviewed by Osburn, Elliott and Martin,[1] and by Goddu and Hume.[2]

In photometric titrations the property studied, in order to obtain the titration equivalence point, is the optical density of the solution. For monochromatic light passing through a solution, the Lambert-Beer Law states that

$$\text{Optical density} = \log \frac{I_0}{I} = kcd$$

where I_0 is the intensity of the incident light, I that of the transmitted light, k is a constant (the absorption coefficient), c is the concentration of the absorbing species and d is the length of the light path. Since photometric titrations are carried out in a vessel for which the length of the light path is constant, the method is based on the simple relationship that the optical density is directly proportional to the concentration of the absorbing species. Changes occur in the concentration of the absorbing species, and hence in the optical density of the solution, during the course of a titration and by interpreting these changes the end-point is obtained.

In most photometric titrations, a plot is drawn of optical density against volume of titrant added, and a study of such a plot gives the end-point. Since the Lambert-Beer Law is only rigidly adhered to for monochromatic light, the most accurate photometric titrations are performed using a spectrophotometer; but many useful titrations may be carried out with a filter photometer. A few titrations have been described where unfiltered light is used but these are the least satisfactory.

The first photometric titrations using a conventional-type photometer were performed by Müller and Partridge[3] in 1928. The potentialities of the method have been greatly increased since use was first made of a spectrophotometer by Goddu and Hume[4] in 1950.

Most photometric titrations fall into one of three classes.

I. *Self-indicator systems*, i.e. *titrations of solutions without the use of an added indicator*

An example of a titration in this class is that of ferrous ions with cobaltic ions[5] (Fig. 1).

Visual titration on solutions in this class can only be performed when either the species being titrated or the titrating substance absorbs very strongly in the visible region of the spectrum, *e.g.* the titration of iodine solutions with thiosulphate ion without the use of starch as an indicator, and the titration of ferrous ions with permanganate ions. In photometric titrations neither reagent need absorb strongly provided that a change in optical density occurs during the course of the titration. Titrations can equally well be made in the ultra-violet and very near infra-red regions of the spectrum. Titrations to maximum turbidity, named heterometric titrations by Bobtelsky,[6] also come into this class.

II. *Titrations in solutions containing more than enough of an indicator to complex, either the substance being titrated, or post-end-point additions of titrant.*

An example is the titration of bismuth with ethylenediaminetetra-acetate in the presence of thiourea as indicator[7] (Fig. 2). The different types of photometric plots for substances in classes I and II are discussed by Goddu and Hume.[2]

III. *Titrations of solutions containing sufficient indicator to complex only a fraction of the substance being titrated, or of the post-end-point additions of titrant. (pH and pM indicators)*

Many recent photometric titrations are in this class. When microgram quantities of a substance are being titrated visually with the use of an indicator it is often observed that sharp end-points are not obtained because the indicator changes colour over a considerable portion of the whole titre. Using a photometric titration excellent results are obtained in these cases.

An example of a titration in this class is that of zinc with ethylenediaminetetra-acetate in the presence of Eriochrome Black T as indicator[8] (Fig. 3).

From what has already been mentioned, it is obvious that photometric titrations have a wide field of application. The method is particularly useful for the titration of coloured solutions since slight changes in optical density, not easily assessed in visual titrations, are readily detected on a photometer. Substances in class I whose reactions are incomplete at the end-point, but complete in the presence of excess of the titrant, can be satisfactorily titrated since the straight portions of the plot well before and well after the end-point may be extrapolated to intersect at the end-point.

Sources of error in photometric titrations

In these titrations, corrections of the optical density readings to constant volume should be made, if the increase in volume of the solution during the titration exceeds 1 %. Otherwise errors in end-point detection will result.

It is also essential to make sure that the titration cell is light-proof with respect to extraneous light. Goddu and Hume[2] have discussed the errors that arise from stray light. In certain cases, the heat of the reaction will increase appreciably the temperature of the solution being titrated and, at times, this may lead to an error in the titration since many absorbing systems are sensitive to temperature changes. In such cases, thermostatically-controlled titration cells may be employed, but for most titrations such a refinement is unnecessary.

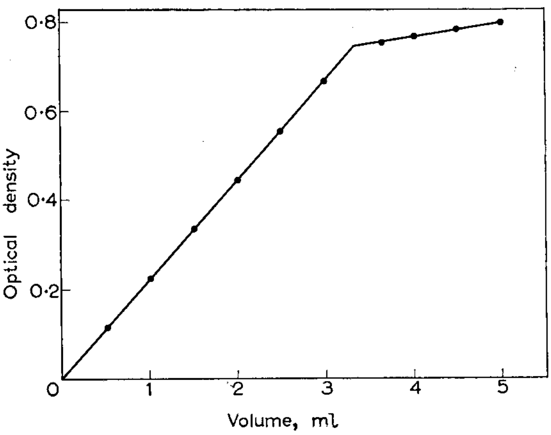

FIG. 1.—Titration of about 1·8 mg of iron^{II} with approx. 0·01M cobalt^{III} sulphate at 360 mμ.

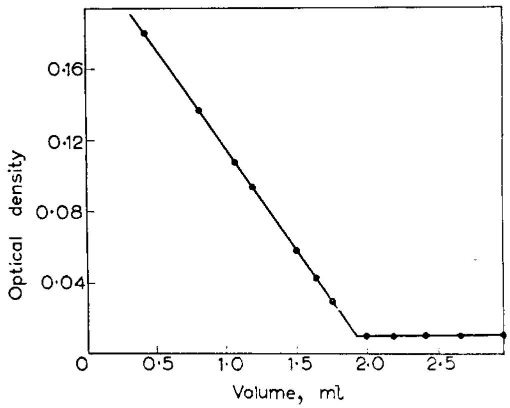

FIG. 2.—Titration of 4·18 mg of bismuth with 0·01M ethylenediaminetetra-acetic acid at 400 mμ (indicator: thiourea).

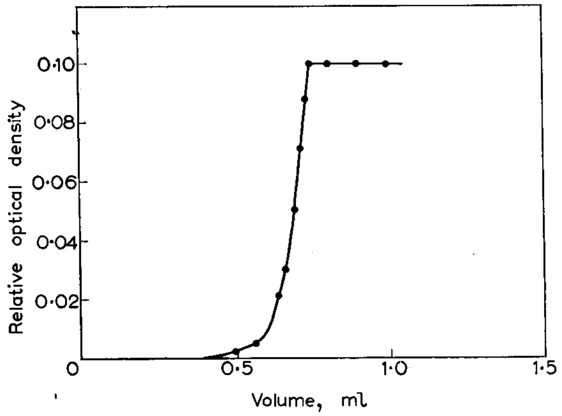

FIG. 3.—Titration of about 100 μg of zinc with 0·0025M ethylenediaminetetra-acetate at 665 mμ (indicator: Eriochrome Black T).

Apparatus

A commercial spectrophotometer is quickly adapted for photometric titrations. For example, Hunter and Miller[8] have modified the Unicam SP 500 and Bricker and Sweetser[9] have converted the Beckman DU for titrations.

REVIEW OF RECENT WORK

Apparatus

Maher[10] has discussed the development of automatic photometric titrimeters. The Beckman Model B spectrophotometer has been modified for automatic titrations.[11] An instrument for automatic derivative spectrophotometric titrations has been described,[12] and Chalmers and Walley[13] have constructed a recording titrimeter.

Stolyarov[14] has described an apparatus for titrations in ultra-violet light where a filter with maximum transmission at 365 mμ is used. Details have been given for the modification of the Beckman DU spectrophotometer for titrations.[15] Wallraf[16] has constructed a filter photometer for the titration of calcium and magnesium with ethylenediaminetetra-acetate.

Review articles and theoretical considerations

Goddu and Hume[2] have discussed the principles of the photometric titration method and have reviewed previous work in the field up to the end of 1953. Underwood[17] has described the advantages of photometric titrations and the application of the method to acid-base, oxidation-reduction, turbidimetric and complexometric reactions.

Grunwald[18] has reported a method for accurate end-point determination in photometric titrations where the titration curves are rounded in the vicinity of the end-point.

Class I titrations

Acid-base: Goddu and Hume[19] have studied the photometric titration of a weak acid (or base) with a strong base (or acid) and have shown that a sharp inflexion of the graph of optical density plotted against volume of titrant is obtained only when the product of ionization constant and molarity of the weak component, is $\geqslant 10^{-12}$ at concentrations of $10^{-5}M$ and above.

Telluric acid has been satisfactorily titrated with aqueous ammonia at 240–280 mμ.[20]

In glacial acetic acid, quinoline, *o*-chloroaniline, *m*-chloraniline and sodium acetate have been titrated photometrically with acetous perchloric acid.[21] Photometric titrations in non-aqueous solvents have so far received little attention. Further investigations in this field could be profitably undertaken.

Oxidation-reduction: Cerous ions in the presence of large amounts of ceric ions in neutral pyrophosphate medium have been determined with permanganate.[22] Cerium, in bismuth-base alloys, can be determined by the titration of the cerium^{III} in pyrophosphate medium with permanganate in the E.E.L. absorptiometer.[23]

Deshmukh and Bapat[24] have titrated thiourea quantitatively in hydrochloric acid-bromide solutions with potassium iodate solution, using a Hilger Spekker absorptiometer for photometric end-point detection.

Sweetser[25] has titrated arsenic^{III} with cerium^{IV} at 320 mμ and, iron^{II} and uranium^{IV}

with cerium^{IV} at 340–360 mμ. The end-point in bromate-bromide titrations has been determined by the absorption of the tribromide ion at 270–360 mμ.[25] Stolyarov[26] has detected the end-point in many titrations by the use of cerium^{IV} and radiation in the region of 365 mμ passing through the solution on to a fluorescent screen. The screen goes dark with one drop of cerium^{IV} in excess.

Iron^{II} has been titrated spectrophotometrically with dichromate at 350 mμ.[27] Bricker and Loeffler[5] have titrated iron^{II}, cerium^{III} and ferrocyanide with cobalt^{III}. Selenite has been determined by reduction with ascorbic acid and photometric titration of excess ascorbic acid with iodine.[28] Dichromate has been titrated with iron^{II} or arsenic^{III}, and vanadate with iron^{II} at 350 mμ.[29]

Complexometric: Magnesium, calcium, zinc and cadmium have been determined by titrating with ethylenediaminetetra-acetate at 222 or 228 mμ.[30] Procedures have been described for the ultra-violet spectrophotometric titration of iron^{III}, copper, nickel and cobalt.[31] Wilhite and Underwood[32] have determined bismuth and lead simultaneously in perchlorate solution by titrating with ethylenediaminetetra-acetate at 240 mμ.

Bertschinger[33] reports that calcium can be determined spectrophotometrically by titration with ethylenediaminetetra-acetate without the use of an indicator. A titration of nickel in the presence of cobalt with ethylenediaminetetra-acetate at 1000 mμ has been described.[34]

Precipitation: In the period 1954–1957, Bobtelsky and co-workers have published a series of papers[6,36–67] on heterometric titrations, *i.e.* titrations to maximum turbidity The first paper by Bobtelsky on such titrations was published in 1953,[35] and he has discussed the fundamental principles of the method.[6]

Magnesium has been determined by titration with 8-hydroxyquinoline in 50% ethanol.[36] Calcium, in the presence of a large excess of magnesium ions and in a strongly ethanolic solution, has been titrated with sulphuric acid.[37] 8-hydroxyquinoline in ethanol or acetic acid solution has been employed to titrate aluminium ions.[38]

A titration of lead with sodium diethyldithiocarbamate has been reported.[39] Bismuth may also be determined with sodium diethyldithiocarbamate.[40] Molybdate in acid solution has been titrated with alcoholic α-benzoinoxime solution.[41]

Iron^{III} has been titrated turbidimetrically with an ethanolic solution of 1-nitroso-2-naphthol[42] and with aluminon (ammonium aurintricarboxylate.[43,44] Cobalt may be determined with an ethanolic solution of 1-nitroso-2-naphthol).[45,46] Palladium^{II} was titrated with 1-nitroso-2-naphthol in ethanol,[47] dimethylglyoxime in ethanol,[48] sodium diethyldithiocarbamate[49] and rubeanic acid (dithio-oxamide).[50]

Copper has been titrated turbidimetrically with 8-hydroxyquinoline in 50% ethanol[51,52] sodium quinaldinate (sodium quinoline-α-carboxylate),[53] salicylaldoxime,[54] sodium diethyldithiocarbamate,[55] and rubeanic acid in ethanol.[56] A solution of *p*-dimethylaminobenzylidinerhodanine has been used to titrate silver ions.[57] Gold may be determined by a turbidimetric titration with sodium diethyldithiocarbamate[49] or rubeanic acid.[50]

Zinc can be titrated with sodium quinaldinate[58] or sodium diethyldithiocarbamate.[59] Cadmium was determined in a titration with sodium diethyldithiocarbamate.[60] Mercury^{II} was titrated heterometrically with mercaptobenzothiazole in ethanol[61,62] and with sodium diethyldithiocarbamate.[63,64] Uranium^{VI} has been titrated turbidimetrically with potassium ferrocyanide solution[65] and with disodium hydrogen phosphate.[66]

Sulphate in an acid solution containing ethanol may be determined by titrating with barium nitrate in 50% ethanol.[67]

Turbidimetric titrations have been used to study the systems, barium sulphate-barium chloride-ethanol-water, barium sulphate-hydrogen chloride-ethanol-water, and barium sulphate-barium chloride-hydrogen chloride-ethanol-water.[68]

Blood-serum proteins have been studied by turbidimetric titration of the serum in a buffer solution with copper and zinc sulphates.[69]

Class II *titrations*

Titanium^{IV} in the presence of hydrogen peroxide has been titrated spectrophotometrically with ethylenediaminetetra-acetate at 450 mμ. The titanium-peroxide complex is converted to a titanium-peroxide-ethylenediaminetetra-acetate complex with a different absorption spectrum, but the method is stated to have few advantages over other existing titrimetric and photometric procedures for titanium.[25,30]

Zirconium has been determined by titration of an added excess of ethylenediaminetetra-acetate with standard iron^{III} in the presence of salicylic acid at 520 mμ.[30] Milner and Edwards[70] have determined zirconium by photometric titration of an excess of ethylenediaminetetra-acetate with iron^{III} using sodium salicylate as indicator in the pH range 3 to 7, and potassium benzohydroxamate in the range 1·8 to 3·3. A similar method has been employed with potassium benzohydroxamate as indicator, to the determination of zirconium in zirconium-uranium alloys[70] and zirconium-cerium alloys.[71] Milner and Barnett[72] also applied the method of back-titrating with iron^{III} to the determination of zirconium in certain ternary alloys.

Thorium has been titrated automatically at 290 mμ with ethylenediaminetetra-acetate in the presence of copper^{II} as indicator.[73] Naphthopurpurin has been employed as an indicator in the photometric titration of thorium with ethylenediaminetetra-acetate.[74] Milner and Sheddon[75] determined thorium by adding an excess of ethylenediaminetetra-acetate and titrating photometrically with thorium perchlorate, eriochrome cyanide being used as indicator. Thorium has also been determined by adding excess ethylenediaminetetra-acetate and back-titrating photometrically with thorium nitrate solution, and with alizarin red S (sodium alizarin sulphonate) as indicator.[76] Banks and Edwards[77] have determined thorium by a procedure based on an initial spectrophotometric titration of a standard ethylenediaminetetra-acetate solution with standard thorium nitrate solution in the presence of Chrome Azurol S as indicator, for the construction of a calibration curve of optical density against volume of thorium nitrate solution added. A solution containing an unknown quantity of thorium is added to the same amount of ethylenediaminetetra-acetate and indicator, as is used for the calibration curve, and the solution is titrated with the standard thorium nitrate solution until the end-point has been passed. The optical density of the solution is then measured, and from the calibration curve, the total quantity of thorium in the solution is found. The unknown quantity of thorium, initially added, is obtained by subtraction.

Bismuth has been titrated with ethylenediaminetetra-acetate at 745 mμ with copper^{II} as indicator. Bismuth is complexed primarily, and, after the end-point, the optical density readings increase as the copper^{II} is complexed.[7] Bismuth may also be titrated spectrophotometrically with ethylenediaminetetra-acetate, in the presence of an excess of thiourea, whose complex with bismuth absorbs strongly at 400 mμ and is broken down in preference to the more stable bismuth ethylenediaminetetra-acetate complex.[7]

Copper^{II} in the presence of ammonia as indicator may be titrated at 630 mμ with ethylenediaminetetra-acetate. The cuprammonium ions, which absorb strongly at 630 mμ are broken down by the ethylenediaminetetra-acetate with the formation of the copper^{II}-ethylenediaminetetra-acetate complex.[78]

Calcium, in strongly ammoniacal solution, has been titrated with ethylenediaminetetra-acetate at 630 mμ, with cuprammonium ions as indicator. Under these conditions, the calcium is first titrated and, only after the end-point of the calcium titration, do the cuprammonium ions react with the ethylenediaminetetra-acetate.[79]

Cyanide, in ammoniacal solution, may be titrated photometrically with silver nitrate in the presence of potassium iodide as indicator.[80]

Fluoride has been titrated photometrically in the presence of sodium alizarin sulphonate, with thorium nitrate solution.[81,82] Hollingworth[83] has determined fluoride by titrating a solution at 580 mμ with thorium nitrate in the presence of sodium 2-(*p*-sulphophenylazo)-1:8-dihydroxy-naphthalene-3:6 disulphonate, which forms a blue-violet lake with excess thorium ions. Dean and co-workers[84] have compared photometric and visual titration techniques for the determination of fluoride using thorium nitrate and alizarin red S indicator.

Class III *titrations*

Acid-Base: A spectrophotometric titration has been employed to determine a mixture of hydrobromic and boric acids with sodium hydroxide as titrant. Methyl red and methyl red-methylene blue indicators were used for the hydrobromic acid and phenolphthalein for the boric acid.[85]

Huguchi, Rehm and Barnstein[86] have shown that endpoints in spectrophotometric titrations can be readily determined by plotting the relative concentration of the acid and basic forms of the indicator in solution against the volume of standard acid or base added or its reciprocal. For systems where $pK_1 \gg pK$ (K is the dissociation constant for the acid or base, and K_1 that of the indicator) the indicator colour-ratio is plotted directly against the volume. For systems where $pK_1 \triangleq pK$, linear plots are only possible if the plots are made against the reciprocal of the volume. The relative concentration of the acid and basic forms of the indicator is found from optical density readings.

A method has been described for the titration of basic substances using weak basic indicators whose colour change occurs primarily after the basic sample has been titrated with an acid. Linear extrapolation of information obtained beyond the end-point gives the stoichiometric value. The method can be applied to the titration of very weak bases, such as aniline, in water, and to the titration of practically non-basic compounds, such as urea, in glacial acetic acid.[87]

Complexometric: Fortuin, Karsten and Kies[88] have evaluated theoretically the conditions for sharp end-points in the titration of bivalent metal ions with ethylenediaminetetra-acetate using murexide as indicator. They are, that the complex-forming capacity of the titrant should be at least 10^4 times greater than that of the indicator, that the complex-forming capacity of the indicator should be large, about 10^4 to 10^5, that the concentration of the indicator should be as low as possible, and that of the substance being titrated as high as possible.

Ringbom and Vanninen[89] have also derived theoretical conditions for the photometric determination of exact equivalence point in the titration of metals with ethylenediaminetetra-acetate using single-colour or two-colour indicators. The principles are illustrated and confirmed experimentally by the titration of copper^{II} with murexide as indicator and the titration of magnesium with Eriochrome Black T as indicator.

Chalmers[90] has determined calcium by spectrophotometric titration at 610 mμ, with ethylenediaminetetra-acetate using murexide as indicator. Calcium in serum and urine has been titrated with ethylenediaminetetra-acetate at 600 mμ with murexide as indicator.[91] Calcium in phosphate solutions has been titrated spectrophotometrically with ethylenediaminetetra-acetate and murexide indicator.[92]

Hoffman and Shapiro[93] have titrated photometrically, calcium and magnesium from agricultural liming materials, using murexide and Eriochrome Black T as indicators, respectively. Ethylenediaminetetra-acetate was the titrant. The theoretical principles for sharp end-points derived by Fortuin and co-workers[88] have been applied to the titration with ethylenediaminetetra-acetate of calcium using murexide or *o*-cresolphthalein complexone as indicator, and of magnesium with Eriochrome Black T or *o*-cresolphthalein complexone.[94]

A circulatory system for the photometric titration of calcium, in the presence of murexide, with ethylenediaminetetra-acetate has been described. The titrant is added to the solution in an external titration cell and a circulatory pump maintains a continuous flow of solution from the titration cell to the flow-through cell of the photometer and back again.[95] Eldjarn *et al.*[96] have titrated serum calcium spectrophotometrically with ethylenediaminetetra-acetate. Calcium and magnesium in carbonate rocks have been determined by automatic titration of calcium with ethylenediaminetetra-acetate and murexide as indicator, and of magnesium with the same titrant and Eriochrome Black T, after the removal of calcium as tungstate.[97]

Horner[98] has determined calcium in biological materials by titration with ethylenediaminetetra-acetate at 620 mμ, murexide being employed as indicator. Calcium in water was determined by spectrophotometric titration with ethylenediaminetetra-acetate, with murexide as indicator.[99] Bertschinger[33] has determined calcium by spectrophotometric titration with ethylenediaminetetra-acetate and an indicator. Campen *et al.*[100] have determined water-soluble calcium in gypsum by titrating the solution photometrically with ethylenediaminetetra-acetate using unfiltered light and murexide as indicator.

Lheureux *et al.*[101] determined calcium and magnesium in rocks and waters by photometric titration with ethylenediaminetetra-acetate using murexide and Eriochrome Black T as indicators. Zak *et al.*[102] have determined calcium and magnesium in spinal fluid by spectrophotometric titration. Calcium is determined in the precipitated oxalate and magnesium in the supernatant liquid by titration at 660 mμ with ethylenediaminetetra-acetate using Eriochrome Black T as indicator.

Serum has been analysed for calcium and magnesium by means of a spectrophotometric titration with ethylenediaminetetra-acetate. Total calcium and magnesium are determined with Eriochrome Black T as indicator and calcium alone with murexide.[103,104]

Rowley *et al.*[105] have titrated barium with ethylenediaminetetra-acetate at 650 mμ

using Eriochrome Black T as the indicator. Barium in the presence of *o*-cresolphthalein complexone, has been determined by photometric titration with ethylenediaminetetra-acetate.[106] Vrestal and Kotrly[107] have studied the possibility of determining lead by photometric titration with ethylenediaminetetra-acetate using Brilliant Congo Blue as indicator. Zinc has been determined by a spectrophotometric titration with ethylenediaminetetra-acetate, Eriochrome Black T being the indicator.[8]

Silver may be determined by adding an excess of potassium tetracyanonickelate^{II} and titrating the liberated nickel, at 440 mμ in the presence of murexide, with ethylenediaminetetra-acetate.[108]

Nitrilotriacetic acid has been determined by photometric titration with copper sulphate solution, either catechol violet or murexide being used as indicator. Large amounts of acid may be titrated without the use of an indicator.[109]

Precipitation: Photometric titrations have been carried out to study the colour change at the end-point of the titration of sulphate with barium chloride using tetrahydroxyquinone indicator. It has been shown that the visual end-point is detected more readily when light, transmitted by a blue filter, illuminates the solution.[110]

Coulometric titrations with spectrophotometric end-points

Wise *et al.*[111] have constructed a ratio-detecting photometer for use in the coulometric titration of acids and bases with photometric detection of the end-point. Photometric end-point detection has been used for the titration of arsenic^{III} with electrically generated iodine.[112] Arsenic^{III} has also been titrated coulometrically with cerium^{IV} in the presence of osmium tetroxide catalyst. The end-point was determined by the absorption of excess cerium^{IV} at 320, 360 or 375 mμ[113]

Malmstadt and Roberts[114] determined vanadium in titanium tetrachloride by hydrolysing the tetrachloride, removing oxygen and chlorine, and titrating the vanadium coulometrically with electrically generated titanium^{III}. The end-point was detected automatically by optical density changes at 490 or 760 mμ. Iron^{III} from titanium sponge has been titrated coulometrically with titanium^{III} generated from the titanium^{IV} in the solution. The end-point is detected spectrophotometrically at 665 mμ by the use of leuco methylene blue indicator. An automatic derivative titrimeter is used.[115]

Titanium in a solution from titanium ores and metal has been determined by passing the solution through a cadmium reductor and collecting the effluent containing titanium^{III} in iron^{III} solution. The excess iron^{III} was titrated coulometrically as in the previous paper.[116] Chromium and iron in titanium can be determined in one titration after oxidation to chromium^{VI} and iron^{III}. Chromium^{VI} is first reduced to chromium^{III} by electrolytically generated titanium^{III}, with diphenylamine sulphonate as indicator for automatic derivative spectrophotometric end-point detection. Iron^{III} is then reduced to iron^{II}, the end-point being detected by means of leuco methylene blue.[117]

Miller and De Ford[118] have determined olefins in glacial acetic-methanol solvent by coulometric titration with bromine generated from potassium bromide and using mercuric chloride as a catalyst. A spectrophotometric end-point was used.

Miscellaneous titrations

Principles, apparatus and procedure have been described for photometric titrations in the ultra-violet region of the spectrum, based on the addition of pure solvent to a concentrated solution until the optical density is exactly equal to that of a known solution. Anthracene is determined in a crude sample by using radiation of 375 mμ and methanol as solvent.[119]

CONCLUSION

The principles of the analytical method of photometric titration have been given. Photometric titrations were classified into three groups, namely (I) titrations in self-indicator systems, (II) titrations in solutions containing more than enough of an indicator to complex, either the substance being titrated, or post-end-point additions of titrant, and (III) titrations in solutions containing sufficient indicator to complex only a fraction of the substance being titrated, or of the post-end-point additions of titrant. An example of the plot of optical density against volume of titrant added, was given for each class of titration. Sources of error in photometric titration and the apparatus used have been discussed. Recent work in the field has been reviewed under the following headings—apparatus, review articles and theoretical considerations, Class I, Class II and Class III titrations, coulometric titrations with spectrophotometric end-points and miscellaneous titrations.

Zusammenfassung—Innerhalb der letzten Jahre wird die photometrische Titration zu einer zunehmend wichtigen Methode. Die Grundsätze der Methode werden besprochen, und die Fehlerquellen kurz erwähnt. Es wird eine umfassende Übersicht der neuen Anwendungen der Technik gebracht.

Résumé—Le titrage photométrique est devenu depuis ces dernières années une méthode analytique d'importance croissante. On discute les principes de la méthode et mentionne brièvement les sources d'erreur. On passe en revue les récentes applications de cette technique.

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A NEW METHOD FOR THE TITRIMETRIC DETERMINATION OF THE FERRICYANIDE ION

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Summary—The direct titration of ferricyanide ions with the mercurous-thiocyanate system is studied, the influence of pH, thiocyanate concentration, time and temperature being considered. The standard deviation of the proposed method is 0·26 per cent.

THE general use of $Hg_2(NO_3)_2$ as a reagent in redox titrations is a relatively recent accomplishment. Bradbury and Edwards, in 1940, proved that in the presence of a great excess of thiocyanate ion, Fe^{3+} can be reduced to Fe^{2+}, and thus mercurous nitrate may be utilised as a reagent for the direct titration of this ion. Later the titration of copper, dichromate, permanganate, cerium, vanadate and other oxidising and reducing agents was proposed.[2]

The mercurous-thiocyanate system has not been applied to the titration of the ferricyanide ion. There is only one determination by the mercurous-iodide system.[3] The present work relates to a study of the direct titration of ferricyanide, utilising mercurous perchlorate as a reagent in the presence of thiocyanate, according to the reaction.

$$2Fe(CN)_6{}^{3-} + Hg_2{}^{2+} + 8SCN^- \rightarrow 2Fe(CN)_6{}^{4-} + 2Hg(SCN)_4{}^{2-}$$

The main inconvenience of this titration is the interferences which can be produced as a result of the reduction of the ferricyanide by the thiocyanate and of the precipitation of mercury ferrocyanide.

In this work the influence of pH, of temperature, of time and of the concentration of thiocyanate are studied, and finally the conditions under which the titration is possible have been determined. The end-point was detected potentiometrically.

EXPERIMENTAL

Apparatus

A Beckman pH-meter, Model G, with a platinum or glass electrode as indicator and a calomel electrode for reference.

Solutions

(1) *Mercurous perchlorate:* 0·1*N*. This salt is used instead of the nitrate because, as indicated by Pugh,[4] of the greater stability of its solutions, which are also almost neutral, and therefore permit a study under better conditions of the influence exercised by acidity. These solutions were prepared in accordance with the method cited by Pugh and modified by S. Arribas.[5]

(2) *Potassium ferricyanide:* 0·1*N*.
(3) *Potassium thiocyanate:* 5*N*.
(4) *Acetic acid:* 5*N*.

THE INFLUENCE OF pH

Titrations were made in the following conditions: (*a*) Sulphuric acid, 0·5*N*; (*b*) Acetic acid, 0·25*N*, pH = 3·0; (*c*) pH = 6·5 (no buffer added), (*d*) Saturated sodium bicarbonate, pH = 8·0; (*e*) Ammonium nitrate–Ammonium hydroxide buffer, pH = 9·2; (*f*) Sodium carbonate, 1%, pH = 10·9; (*g*) Sodium hydroxide, 0·5*N*.

In each case the pH value of the solution to be tested was first measured electrometrically by a glass electrode.

PROCEDURE

Different volumes of ferricyanide solution were taken, the calculated quantity of the substance for regulating the pH value of the solution was added, and the solution was then diluted to 100 ml. Finally, 20 ml of 5*N* KSCN were added and the solution was titrated with mercurous perchlorate solution. During titration, the solution was stirred mechanically. The results obtained are shown in Table I.

TABLE I

pH conditions	Ferricyanide taken, *meq*	$Hg_2(ClO_4)_2$ 0·1117*N*, *ml*	Ferricyanide found, *meq*	Diff., *meq*	Diff., %
a	2·355	20·75	2·318	−0·037	−1·5
b	2·372	21·20	2·368	−0·004	−0·2
c	2·385	21·35	2·385	—	—
d	2·372	21·05	2·351	−0·021	−0·9
e	2·372	20·90	2·335	−0·037	−1·8
f	2·385	21·05	2·351	−0·034	−1·4
g	2·385	—	—	—	—

Remarks

When titration in acid medium is halfway completed, a green intermediate compound is formed which later disappears and has no influence on the final result. This compound, whose nature has not been defined, is more easily formed, the greater the ferricyanide concentration of the solution to be tested.

In alkaline medium, the precipitate formed at the beginning of the titration is of a slightly reddish-brown colour, probably due to the transitory formation of some HgO, or of mercury ferrocyanide or ferricyanide, together with metallic Hg. There is no formation of an intermediate green compound.

Potentiometric measurement indicates at the end-point, on the addition of a single drop of mercurous reagent, a jump in the potential that varies between 100 mV and 60 mV. This potential jump decreases with increasing concentration of the solution: for which reason the quantity of ferricyanide present should therefore not exceed 2·3 meq for each 100 ml of solution. The potential is rapidly stabilised, except near the end-point, where the reaction is rather slow, so that one minute is required after each addition of perchlorate. The potential change, even in the most unfavourable cases, is quite perceptible.

At the beginning of a titration in 0·5*N* NaOH, a drabbish-black precipitate is obtained, which does not disappear despite violent stirring. The reduction which occurs, although only slight, decreases the potential of the system in a variable manner, so that titration of ferricyanide under such conditions is not possible.

By a study of the Table I, it appears that the pH value at which the titration should be carried out must not be less than 3 or greater than 7. Tests were made varying the quantity of acetic acid from 1 to 20 ml, and similar results were obtained in all cases.

THE INFLUENCE OF THIOCYANATE CONCENTRATION

Procedure

At a fixed pH (acetic acid medium) the amount of thiocyanate was varied, operating as described above. The results obtained are shown in Table II.

Remarks

Where the thiocyanate concentration is less than or equal to 0·5*N*, and the amount of ferricyanide is more than 2 meq, an early appearance of a precipitate will cloud the solution. This first is dark green, becoming darker and changing to navy blue. The solution at the end-point is decolorised and has a yellow-greenish tint.

The potential jump is more clearly defined, the greater the thiocyanate concentration. From these results, the concentration used in subsequent work was 20 ml of 5*N* KSCN for each 100 ml of solution, representing a 1*N* concentration of SCN^-.

TABLE II

KSCN concentration	Ferricyanide taken, *meq*	$Hg_2(ClO_4)_2$ 0·1117*N*, *ml*	Ferricyanide found, *meq*	Diff., *meq*	Diff., %
0·25*N*	2·385	21·00	2·346	−0·039	−1·6
—	0·949	8·50	0·949	—	—
0·50*N*	2·385	21·15	2·362	−0·023	−1·0
—	0·949	8·45	0·943	−0·006	−0·6
0·75*N*	2·385	21·25	2·373	−0·012	−0·5
—	0·949	8·50	0·949	—	—
1·0*N*	2·372	21·15	2·362	−0·010	−0·4
—	0·949	8·50	0·949	—	—

INFLUENCE OF TIME

In the earlier experiments titration was carried out immediately after adding the KSCN to the mixture of ferricyanide and acetic acid. In order to check on a possible secondary reaction between the ferricyanide and the thiocyanate, variable lengths of time were allowed to pass between the addition of KSCN and titration.

TABLE III

Time interval	$Hg_2(ClO_4)_2$ 0·1117*N* *ml*	Ferricyanide found, *meq*	Diff., *meq*	Diff., %
0	16·85	1·882	−0·002	−0·1
5 min	16·75	1·871	−0·013	−0·6
10 min	16·70	1·865	−0·019	−1·0
15 min	16·75	1·871	−0·013	−0·6
30 min	16·70	1·865	−0·019	−1·0
60 min	16·65	1·860	−0·024	−1·3
2 hr	16·65	1·860	−0·024	−1·3
4 hr	16·60	1·854	−0·030	−1·6
6 hr	16·55	1·849	−0·035	−1·9
12 hr	16·50	1·843	−0·041	−2·2
24 hr	16·35	1·826	−0·058	−3·1
48 hr	16·10	1·798	−0·086	−4·5

Procedure

In all cases 20 ml of 0·0942*N* ferricyanide, 5 ml of 5*N* acetic acid and 20 ml of 5*N* KSCN were used. The lapse of time between the addition of the thiocyanate and the beginning of the titration was measured. The results are shown in Table III.

Remarks

With passage of time a gradual reduction of ferricyanide takes place; acetic acid or neutral solutions change their yellow colour, and within two hours acquire a slight olive tint which, after six hours changes to green and within twenty-four hours to very dark green.

On the other hand, alkaline solutions allowed to stand for the same length of time do not change in appearance, although when titrated they also show a decrease in ferricyanide concentration.

The reduction to which the solutions are subject after a certain length of time offers no great inconvenience, as it can be overcome by adding the thiocyanate immediately before the beginning of the titration.

TABLE IV

Temperature °C	$Hg_2(ClO_4)_2$ 0·1117*N*, *ml*	Ferricyanide found, *meq*	Diff., *meq*	Diff., %
15°	16·85	1·882	−0·002	−0·1
20°	16·75	1·871	−0·013	−0·6
25°	16·65	1·860	−0·024	−1·3
30°	16·40	1·832	−0·052	−2·7
45°	16·00	1·787	−0·097	−5·2

INFLUENCE OF TEMPERATURE

In order to determine whether an increase of temperature favours the reaction between the ferricyanide and the thiocyanate, tests were made at various temperatures.

Procedure

The solutions were independently heated before being mixed. On mixing the solutions at temperatures over 25°, they became dark green in colour. The amount of ferricyanide used was 1·884 meq. The results are shown in Table IV.

Remarks

At temperatures over 20° there is an appreciable reduction of ferricyanide.

Other experiments in the present work were carried out at a temperature of 14° ± 1°.

RECOMMENDED METHOD

The solution, containing 0·4 to 3 meq. of ferricyanide is treated with 5 ml of acetic acid, diluted to 100 ml and treated with 5 ml of 5*N* acetic acid and 20 ml of 5*N* KSCN. It is immediately titrated at ordinary temperature (less than 20°) with mercurous perchlorate, the end-point being detected potentiometrically.

Specimen results are shown in Table V.

CONCLUSIONS

In the direct titration of ferricyanide with mercurous perchlorate in the presence of thiocyanate ion, it is found that:

1. The satisfactory pH range is from 3 to 7. Outside this range lower results are obtained, probably because part of the ferricyanide is reduced by the thiocyanate ion.

2. The lowest optimum concentration of thiocyanate ion is 1*M*, at which concentration the potential jump at the end-point is large and correct results are obtained. On decreasing the SCN^- concentration, the potential jump gradually becomes smaller.

3. A secondary reaction occurs between ferricyanide and thiocyanate. If the ferricyanide and the thiocyanate solutions are mixed immediately before the beginning of the titration this does not affect the results.

4. At temperatures over 20° there is an appreciable and immediate reduction of ferricyanide.

5. Direct mercurometric titration of ferricyanide in the presence of thiocyanate ion is possible in conditions which have been established. The standard deviation of the method is 0·26%.

TABLE V

Ferricyanide taken, *meq*	$Hg_2(ClO_4)_2$ 0·1117*N*, *ml*	Ferricyanide found, *meq*	Diff., *meq*	Diff., %
2·847	25·50	2·848	+0·001	+0·04
2·372	21·15	2·362	−0·010	−0·4
1·898	16·95	1·893	−0·005	−0·3
1·423	12·75	1·424	+0·001	+0·1
0·949	8·50	0·949	—	—
0·474	4·25	0·475	+0·001	+0·2

Zusammenfassung—Die direkte Titration von Ferricyanid-Ionen mit dem Merkurothiocyanat-System wird studiert und der Einfluss von pH, Thiocyanat-Konzentration, Zeit und Temperatur untersucht. Die Standard-Abweichung der vorgeschlagenen Methode beträgt 0,26%.

Résumé—On étudie le titrage direct des ions ferricyanhydriques par le système du thiocyanate-mercureux, compte tenu de l'influence du pH, de la concentration du thiocyanate, du temps, de la température. L'écart-type de la méthode proposée est 0,26 pour cent.

Resumen—Se estudia la volumetria directa del ion ferricianuro con el sistema mercurioso-sulfocianuro, viendose la influencia del pH, concentración de sulfocianuro, tiempo y temperatura. La desviación típica del método propuesto es 0,26%.

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TITRIMETRIC DETERMINATION OF SMALL AMOUNTS OF COBALT WITH AN EQUIVALENT RATIO OF 1 : 37

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Summary—The nitrite content of the $KPb[Co(NO_2)_6]$ precipitate has been determined by reducing nitrite with excess of Fe^{II} salt. The excess of Fe^{II} or the Fe^{III} formed was then determined. With an equivalent ratio of 1 : 37 an exact method could thus be obtained for the titrimetric determination of small amounts of cobalt.

THE cobaltinitrite method is suitable for the titrimetric determination of both potassium and cobalt. The first requirement for the determination of cobalt is a well defined *ratio* of Co^{III} and NO_2^-. On the other hand for the determination of potassium a definite *composition* of precipitate is necessary. In the determination of cobalt where potassium is in great excess, the composition of precipitate is exactly $K_3[Co(NO_2)_6]$. In the determination of potassium the composition of precipitate varies with the conditions of precipitation, the ratio K : Na deviating more or less from the value of 2 : 1. Nevertheless, numerous methods have been elaborated for the determination of potassium but there are only a few procedures for cobalt. A plausible reason for this is that the analytical chemistry of potassium is not so extensive as that of cobalt. Among cobaltinitrite methods for the determination of cobalt, only one is generally applied, viz. permanganometric titration of nitrite content of the precipitate. In this method the equivalent weight of cobalt is 1/11 of the atomic weight, a ratio rendering possible the determination of small amounts of cobalt.

The present work aims to develop this method, but the nitrite content of the precipitate was determined by a method with an equivalent ratio of 1 : 37 which is very advantageous for the determination of small amounts of cobalt.

Recently, a procedure for the titrimetric determination of nitrate ions was reported.[1] In this procedure ferrous hydroxide reduces nitrate to ammonia in a slightly alkaline medium, in the presence of silver catalyst:

$$KNO_3 + 8Fe(OH)_2 + 6H_2O \rightarrow NH_3 + 8Fe(OH)_3 + KOH$$

The excess of the reducing agent is back-titrated.

The reduction of nitrite also takes place rapidly without a catalyst:

$$KNO_2 + 6Fe(OH)_2 + 5H_2O \rightarrow NH_3 + KOH + 6Fe(OH)_3$$

From these equations the equivalent ratios of nitrate and nitrite are 1/8 and 1/6 of the ionic weight, respectively.

Consequently, the determination of the nitrite content of the potassium cobaltinitrite precipitate by the above method, gives an unusually low equivalent weight of cobalt: for the reduction of six nitrites 36 equivalents, and for the reduction of Co^{III} 1 equivalent of Fe^{II} is consumed; thus the equivalent weight of cobalt is 1/37 of the atomic weight.

The precipitate $2K_3[Co(NO_2)_6]\cdot 3H_2O$ is slightly soluble in water; the solubility decreases in alcoholic or dilute acetic acid medium. The solubility of the precipitate can be further decreased if potassium is partly substituted by heavy metals.

Precipitates of $K_2Ag[Co(NO_2)_6]$ and $KPb[Co(NO_2)_6]$ have the lowest solubility, the latter being more soluble.[2] The ratio of K : heavy metal is in neither case stoichiometric,[3] but this is not important since the cobalt : nitrite ratio is constant. According to the view of a number of authors the most suitable reagent for potassium is silver cobaltinitrite. However, the $K_2Ag[Co(NO_2)_6]$ precipitate cannot be used for the determination of cobalt because silver ion also forms a precipitate with nitrite ion. Conversely, the great solubility of lead nitrite renders the precipitation of potassium lead cobaltinitrite possible.

The precipitation was therefore carried out in the presence of lead salt. This has also the advantage that the analysis of the precipitate can be performed after one hour, since the quantitative precipitation takes place much more rapidly than in the absence of lead.

The determinations were carried out on a $Co(NH_4)_2(SO_4)_2\cdot 6H_2O$ solution. Because of the large excess of lead, lead sulphate also precipitates. According to our observations, the co-precipitated lead sulphate influences the form of $KPb[Co(NO_2)_6]$ favourably and consequently the sedimentation and washability of the precipitate. Therefore, if none be originally present it is useful to add a small amount of sulphate ions. The presence of larger amounts of lead sulphate is, however, disadvantageous, because the precipitate becomes rather flocculent and its washing is difficult.

To separate the precipitate the solution was centrifuged. The precipitation was consequently carried out in centrifuge tubes. The precipitate was washed with saturated potassium sulphate solution in which the solubility of the precipitate is very low; in addition, the sulphate ions displace adsorbed nitrite ions.

After washing, the precipitate was treated with sodium hydroxide, which decomposes the complex:

$$KPb[Co(NO_2)_6] + 7NaOH \rightarrow KNO_2 + 5NaNO_2 + Co(OH)_3 + Na_2PbO_2 + 2H_2O$$

EXPERIMENTAL

Depending on the quantity of cobalt the determination was carried out in one of two ways. In the case of 0·3–3 mg of Co the excess of ferrous salt was back-titrated by 0·1*N* potassium permanganate. When the amount of cobalt is less than 0·3 mg, and using 0·01*N* potassium permanganate for the titration, the accuracy is not satisfactory. Therefore in such cases iodometric titration was used. The reduction was carried out by ferrous salt, and the Fe^{III} formed was determined iodometrically. 0·01*N* sodium thiosulphate was used as standard solution.

Solutions

Acetic acid: 96%

Lead acetate: 180 g $Pb(CH_3COO)_2\cdot 3H_2O$ per litre.

Potassium nitrite: 1000 g KNO_2 per litre.

Potassium sulphate: saturated solution.

Sodium hydroxide: 30% solution.

Ferrous sulphate: 135 g $FeSO_4\cdot 7H_2O$ and 30 ml conc. sulphuric acid per litre.*

Sulphuric acid: 30% solution.

Hydrochloric acid: 4*N*

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* In the case of a micro method it is essential that the Fe^{III} content of Fe^{II} is kept small, because in this case the Fe^{III} is measured. The presence of small amounts of Fe^{III} does not interfere, and the amount of Fe^{III} must be determined as a blank.

Potassium permanganate: 0·1*N*
Sodium thiosulphate: 0·01*N*

Procedure for determination of 0·3–3 mg Co

5 Ml of a neutral solution of cobalt salt are introduced into a centrifuge tube. If the solution does not originally contain sulphate ions, potassium sulphate should be added in a quantity such that the equivalent ratio of the sulphate ions to Co expected is about 1 : 4. To this solution 0·3 ml of acetic acid, 1 ml of lead acetate solution and finally 1 ml of potassium nitrite solution are added. After standing for an hour the mixture is centrifuged for 20 minutes at 3000 rpm. The precipitate is washed three times by 3 ml of saturated potassium sulphate solution. For each portion of the wash solution 10 minutes centrifugation is carried out. After washing, the precipitate is transferred with 90 ml of water into a 250-ml flask. After the addition of 10 ml of 30 % NaOH the mixture is boiled for 10 minutes to remove air and to decompose the complex. Thereafter, keeping the mixture boiling, 10 ml of ferrous sulphate solution are added. A mouthpiece is then adjusted in the neck of the flask[1] to avoid air passing easily into the flask, and to inhibit too rapid evaporation of the solution.

TABLE I.

Co taken *mg*	Consumption of 0·1*N* $KMnO_4$ *ml*	Co found *mg*	Error %
2·872	17·99	2·866	−0·2
	17·92	2·855	−0·6
	17·84	2·842	−1·0
1·436	8·99	1·432	−0·3
	9·04	1·440	+0·3
0·574	3·60	0·573	−0·2
	3·58	0·570	−0·7

Co taken *μg*	Consumption of 0·01*N* $Na_2S_2O_3$ *ml*	Co found *μg*	Error %
295·3	18·75	298·8	+1·2
	17·77	283·1	−4·1
	17·80	283·6	−4·0
147·6	8·90	141·8	−3·9
	9·07	144·4	−2·2
	8·88	141·5	−4·1
103·3	6·14	97·8	−5·3
	6·63	108·1	+4·6
44·3	2·65	42·2	−4·7
	2·80	44·6	+0·7
	2·70	43·1	−2·7

The time for complete reduction is 3–6 minutes. (The odour of ammonia vanishes.) Then 40 ml of sulphuric acid are carefully added to the flask through the mouthpiece. When the precipitate has completely dissolved the boiling should be stopped, and after cooling, the unoxidized ferrous salt is titrated by 0·1*N* $KMnO_4$.

A blank determination must also be carried out. The difference between the blank and the sample gives the volume of 0·1*N* $KMnO_4$ actually used. 1 ml 0·1*N* $KMnO_4 \equiv$ 0·1593 mg cobalt.

Procedure for determination of 30–300 μg Co

To 2 ml of neutralized test solution 0·2 ml of acetic acid, 0·5 ml of lead acetate solution and 0·5 ml of potassium nitrite solution are added. If the solution does not contain sulphate, potassium sulphate must also be added as before. The contents of the centrifuge tube are stirred and after standing for an hour, are centrifuged for 10 minutes. The precipitate is washed three times by 3 ml of potassium sulphate solution, and each portion is centrifuged for 5 minutes. The precipitate is transferred to a 100-ml flask with 25 ml water followed by 5 ml of 30% sodium hydroxide; after 5 minutes boiling, 5 ml of ferrous sulphate solution are added. After 5 minutes further boiling, 20 ml of 4*N* hydrochloric acid are added to the flask. A few pieces of marble are then placed in the solution. After cooling the solution to 40–50°, and addition of 5 g* potassium iodide, the iodine formed is titrated by 0·01*N* thiosulphate.

In this method a blank is also required. 1 ml 0·01*N* $Na_2S_2O_3 \equiv$ 15·93 μg cobalt.

The results of some titrations are summarized in Table I.

As Table I shows the error of the determination by the macro method is about ±1%, and that of the micro method about ±5%. The micro method makes the determination of less then 40 μg Co possible, but in this case the error increases with decreasing amount of Co.

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Zusammenfassung—Der Nitritgehalt des $KPb[Co(NO_2)_6]$-Niederschlages wird über die Reduktion des Nitrits mit einem Uberschuss von Fe(II)-Salz bestimmt, wobei der Uberschuss von Fe(II) oder das gebildete Fe(III) erfasst wird. So konnte bei einem Aquivalent-Verhältnis von 1 : 37 eine genaue Methode für die volumetrische Bestimmung kleiner Mengen von Kobalt erhalten werden.

Résumé—La teneur en nitrite du précipité $KPb[Co(NO_2)_6]$ a été déterminée par la réduction du nitrate par un excès de Fe(II). On a effectué ensuite le dosage de l'excès de Fe(II) ou du Fe(III) formé. Le rapport équivalent 1 : 37 a permis d'obtenir une méthode exacte pour le dosage volumétrique de petites quantités de cobalt.

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* The completion of the reaction: $Fe^{3+} + I^- \rightleftharpoons Fe^{2+} + 1/2\ I_2$ in the forward direction requires a large amount of KI because of the large excess of Fe^{II}.

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TITRIMETRIC DETERMINATION OF ALUMINIUM WITH ETHYLENEDIAMINETETRA-ACETIC ACID IN THE PRESENCE OF IRON, COPPER, TITANIUM, MANGANESE, CALCIUM, MAGNESIUM AND PHOSPHATE

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Summary—The authors have developed a rapid and accurate titrimetric method for the determination of 5–15 mg of aluminium with Complexone-III in the presence of iron, copper, titanium, manganese, calcium, magnesium and phosphate.

INTRODUCTION

IN THE research undertaken for the enrichment of certain raw materials such as manganese ores, clays and feldspars in Israel Mining Industries Laboratories, a rapid method was needed for the determination of aluminium in the above mentioned materials.

In the literature some complexometric methods were found for the determination of aluminium when present alone,[1–12] and also for a few cases when it is present together with other ions[13–16] but here either the analytical results were insufficiently accurate or the methods were complicated. It was therefore decided to essay to develop a complexometric method for the determination of aluminium in the presence of iron, copper, titanium, manganese, calcium, magnesium and phosphate.

The research was done in several steps: in the first one, the optimum conditions for the determination of aluminium, when present alone, were determined, taking into account the methods found in the literature and their experimental verification; in the next step, a method for the determination of aluminium in the presence of iron, copper and phosphate was elaborated; in the third step, a cation-exchange method was established for the separation of aluminium from titanium, manganese, calcium and magnesium; a general procedure was then developed for the determination of aluminium in the presence of all the above mentioned ions, considering the minimum time requirement; finally the maximum allowable quantity of the above mentioned ions that can be present, without impairing the accuracy of the aluminium determination, was determined. The results of this research are given below.

PART I: THE DETERMINATION OF ALUMINIUM WHEN PRESENT ALONE

Reagents and standard solutions

1. *Aluminium sulphate solutions:* Aluminium sulphate was dissolved in distilled water and the solution was then made distinctly acidic with hydrochloric acid (around 3*N*) to prevent hydrolysis on long standing. From this rather concentrated solution (about 10 mg aluminium per ml) lower concentrations were prepared by dilution after standardisation.

The standardisation was done by two methods: (*a*) Gravimetrically by ammonia precipitation and ignition to the oxide[17] and (*b*) Gravimetrically with 8-hydroxyquinoline.[18] The mean value was 9·026 mg Al/ml.

2. 0·01M *solution of Complexone-III*: (the disodium salt of ethylenediaminetetra-acetic acid, dihydrate, abbreviated as EDTA): prepared by dissolving 3·722 g of Complexone-III in twice-distilled water and making the total volume up to one litre. The solution can be standardised against either 0·01M solution of magnesium chloride or 0·01M solution of zinc chloride, using Eriochrome Black T as indicator. Accurate concentrations of either may be prepared from magnesium and zinc metal respectively, as primary standards.

3. 0·01M *solution of zinc chloride:* prepared by dissolving 1·363 g of anhydrous zinc chloride in twice distilled water and making the total volume up to one litre.

Using the above 0·01M solution of EDTA, we standardised the 0·01M solution of zinc chloride at pH 6·7–7·3 as follows:—Into an Erlenmeyer flask of 250-ml capacity 25 ml of 0·01M solution of EDTA, 10 ml of ammonium acetate solution 10%, a little Eriochrome Black T indicator and 80–100 ml of distilled water were introduced. The solution was then titrated with the 0·01M zinc chloride solution till the colour of the indicator changed from blue to bluish-violet. The colour change is sharp and easily seen on addition of one drop of the titrant.

The factor for the same zinc chloride solution is different when the titration is done at pH 6·7–7·3 and at pH 10. Since the aluminium will be determined by the back-titration of the excess EDTA at pH 6·7–7·3, the standardisation of the zinc chloride solution must also be done at pH 6·7–7·3.

4. *Eriochrome Black T indicator:* 0·1 g triturated with 10 g of sodium chloride.
5. *Methyl red indicator:* 0·1 g dissolved in 100 ml of ethanol 50%.
6. *Ammonium acetate solution:* 10%.
7. *Ammonia solution:* 5%.

Procedure "A" for the determination of aluminium

The slightly acidic solution of the sample, containing 5–10 mg of aluminium in a volume of 5–10 ml, is introduced into a Pyrex 250-ml Erlenmeyer flask. A known excess of 0·01M solution of EDTA is added, followed by one drop of methyl red indicator. Ammonia solution 5% is then added with shaking, till the solution turns from red to yellow. The solution is then boiled for three minutes, cooled to below 10°, and 10 ml of ammonium acetate solution 10% are added, followed by a little Eriochrome Black T. The excess of EDTA is now back titrated with 0·01M solution of zinc chloride till the colour of the indicator turns from blue to bluish-violet.

Calculation of the results

$$A = (BC - DE)(0{\cdot}2697)$$

where: A = mg Al found.
B = ml 0·01M solution of EDTA added.
C = the factor of the EDTA solution.
D = 0·01M solution of $ZnCl_2$ required for the back-titration.
E = the factor of the $ZnCl_2$ solution.
0·2697 = the factor for aluminium.

Table I shows some typical results obtained according to the above mentioned method.

Conclusion

As indicated by Table I, the results are accurate.

Discussion

1. In the light of the literature data and the experimental checks which we have made on few complexometric methods for the determination of aluminium, using various indicators such as Eriochrome Black T,[1,7] Chromazurol S,[6] dithizone,[10] ferro-ferricyanide + benzidine,[14] 1-(2-pyridylazo)-2-naphthol (PAN),[15] salicylic acid,[4] to mention but a few, we chose Eriochrome Black T as the indicator in our research. Schwarzenbach and Biedermann[19] were the first to suggest the use of this indicator for complexometric titrations. In spite of the interference of aluminium when using Eriochrome Black T,[20] we concluded, nevertheless, that it is the most suitable for our purpose.

2. Boiling the solution with excess EDTA is necessary if we have to chelate the aluminium quantitatively.

3. It is necessary to cool below 10° when titrating the excess EDTA in order that the end-point be reversible. (Table I, Exp. 5–7).

4. Aluminium chelate is unstable at pH 10 in the absence of excess free EDTA (as it is the case at the end-point), so that during the back-titration of the excess EDTA the aluminium chelate decomposes to yield free EDTA, causing the red colour to turn to blue. Although Amin[7] suggests that the back-titration should be done very quickly, nevertheless, a large error was obtained, even through a quick titration, since the colour returned after a few seconds. We decided, therefore, to titrate the excess of EDTA at pH 6·7–7·3 instead of at pH 10, since at the former pH value the aluminium chelate is more stable.

TABLE I. DETERMINATION OF ALUMINIUM WITH EDTA ACCORDING TO PROCEDURE "A", UNDER VARIOUS CONDITIONS

Exp. no.	Time of boiling with excess of EDTA *minutes*	Temperature during the back-titration of EDTA °C	Al present *mg*	Al found *mg*	Difference *mg*	Rel. error %	Notes
1	3	25	4·513	4·526	+0·013	+0·3	*
2	5	25	4·513	4·520	+0·007	+0·2	*
3	15	25	4·513	4·509	−0·004	−0·1	*
4	15	25	4·513	4·522	+0·009	+0·2	*
5	15	0	4·513	4·520	+0·007	+0·2	†
6	3	0	4·513	4·525	+0·012	+0·3	†
7	3	10	4·513	4·522	+0·009	+0·2	†

* Irreversible end-point.
† Reversible end-point.

Although accurate results were obtained according to procedure "A", the method is a back-titration one and any metal ion chelated by EDTA at pH 6·7–7·3, such as ferric or cupric ion, would give a high result for aluminium. In other words this procedure is applicable only for pure aluminium compounds.

It was thought therefore, that if a reagent were found that could liberate, under our conditions, free EDTA from its chelate with aluminium but had no effect on the chelates of other metals, then this liberated free EDTA, which is proportional to the quantity of aluminium in the sample, might be estimated through simple titration with a standard solution of zinc. The applications of the method would thus be more general.

Triethanolamine, a known masking agent for aluminium in complexometric titrations,[21,22] was tried. We also tested oxalate, tartrate and citrate. It was found that none of these compounds liberate EDTA from the aluminium chelate at pH 6·7–7·3. Sodium fluoride was then examined for this purpose.

Sajo[14] determines aluminium, after the addition of excess EDTA and back-titration of the excess, by the addition of sodium fluoride and the titration of the EDTA, liberated from the aluminium chelate, at pH 5–6·7 with a standard solution of zinc, using ferro-ferricyanide + benzidine as indicator.

In order to examine the use of sodium fluoride under our conditions, procedure "A" was modified into procedure "B".

Procedure "B" for the determination of aluminium

To the bluish-violet solution, obtained after back-titration of the excess EDTA, 1·5 g of sodium fluoride is added, the solution is kept at 90° for 20 minutes, cooled to below 10°, and the liberated EDTA is titrated with 0·01M standard solution of zinc to the same end-point of Eriochrome Black T.

If this liberation of EDTA is quantitative, then the quantity of the zinc solution used will be a measure of the quantity of aluminium in the sample. Table II shows some of the results obtained according to this procedure.

Conclusion

As indicated by Table II, the results are accurate. At pH 6·7–7·3 the liberation of EDTA from the aluminium chelate by sodium fluoride is quantitative. This offers an indirect method for the determination of aluminium.

Note: It should be noted that the addition of sodium fluoride does not alter the pH of the solution (pH 6·7–7·3). This is important, since any change in the pH of the solution after the back-titration of the excess EDTA affects the accuracy of the method.

TABLE II. DETERMINATION OF ALUMINIUM WITH EDTA ACCORDING TO PROCEDURE "B"

Exp. No.	Al present *mg*	Al found *mg*	Difference *mg*	Relative error %
1	4·513	4·509	−0·004	−0·1
2	4·513	4·524	+0·011	+0·2
3	4·513	4·501	−0·012	−0·3
4	9·026	9·048	+0·022	+0·2
5	9·026	9·007	−0·019	−0·2

The next step was to investigate the behaviour of iron in the determination of aluminium, according to procedure "B".

The behaviour of iron in the determination of aluminium, according to procedure "B"

Early experiments showed that even less than 0·2 mg of ferric iron interferes, since it forms a very stable chelate (brownish-black precipitate) with Eriochrome Black T. This interference could not be prevented by adding fluoride, oxalate, tartrate, citrate, etc., as masking agents. It was thought possible to get rid of the interference of ferric iron by reducing the former to the bivalent state. Various reducing agents, such as ascorbic acid, hydrazine sulphate, hydroxylamine hydrochloride and sulphite were tried at pH 6·7–7·3. But, when excess EDTA was added, the solution slowly turned yellow, indicating air oxidation and formation of ferric chelate, even in the presence of a large excess of the reducing agent. Finally it was thought that an alcoholic medium might alter the formation constant of ferric iron with Eriochrome Black T. It was found that this chelate is so weak in the presence of alcohol that the interference of iron is eliminated. By conducting the titration in alcoholic medium, the optimum condition for a sharp colour change was found to correspond to about 40% of alcohol in water. No difference was found by using *iso*propyl alcohol instead of ethyl alcohol. The back-titration method according to procedure "A" was now applied to a pure standard solution of iron. (Table III, Exp. 1). The determination was then repeated adding 1·5 g of sodium fluoride to the solution after boiling with excess EDTA, *i.e.* before proceeding to determine aluminium according to procedure "B" (Table III, Exp. 2). The results obtained are shown in Table III.

Conclusions

1. Ferric iron behaves like aluminium in that it is quantitatively chelated by EDTA and therefore aluminium cannot be determined according to procedure "A" in presence of iron, in which case procedure "B" should be followed.

2. Ferric-EDTA chelate, unlike the aluminium chelate, is not affected by fluoride, since it is more stable than the ferric fluoride complex; thus ferric iron does not interfere in the determination of aluminium according to procedure "B".

TABLE III. DETERMINATION OF FERRIC IRON ACCORDING TO PROCEDURES "A" AND "B" FOR DETERMINATION OF ALUMINIUM

Proc.	Exp. No.	Conc. of alcohol used %	Temp. at which the titration was done °C	Fe^{3+} present *mg*	Fe^{3+} found *mg*	Diff. *mg*	Rel. error %	Notes
A	1	40	8–10	5·819	5·807	−0·012	−0·2	reversible end-point
B	2	40	8–10	5·819	5·830	+0·011	+0·2	

PART II: DETERMINATION OF ALUMINIUM IN THE PRESENCE OF IRON, COPPER AND PHOSPHATE

Reagents and standard solutions

1. *0·05M solution of Complexone-III (EDTA)*: prepared by dissolving 18·610 g of Complexone-III in twice distilled water and making the total volume up to one litre.
2. *0·01M solution of Complexone-III (EDTA):* (See Part I, reagent no. 2).
3. *0·05M solution of zinc chloride:* prepared by dissolving 6·815 g of anhydrous zinc chloride in distilled water and making the total volume up to one litre.
4. *0·01M solution of zinc chloride*: (See Part I, reagent no. 3).
5. *Ammonia solution:* 5%.
6. *Ammonium acetate solution:* 10%.
7. *Sodium fluoride.*
8. *Methyl red indicator.* (See Part I, reagent no. 5).
9. *Eriochrome Black T indicator.* (See Part I, reagent no. 4).

Procedure for the determination of aluminium in the presence of iron, copper and phosphate

The solution of the sample, in a volume of around 5 ml and containing not more than 15 mg of aluminium, is introduced into a Pyrex 250-ml Erlenmeyer flask. From a burette 0·05*M* solution of EDTA is introduced in such an amount as to be in excess to that required to chelate the aluminium, iron and copper in the sample. A very large excess should be avoided. 1–2 Drops of methyl red indicator are added. With distilled water the total volume is then brought to about 20 ml, followed by the dropwise addition of ammonia solution 5%, with constant shaking, until the colour of the indicator turns from red to yellow. The solution is then boiled for three minutes, cooled, 10 ml of ammonium acetate 10% are added, followed by 25 ml of *iso*propyl alcohol, and distilled water to make the total volume up to approximately 60–65 ml. The solution is then cooled in ice-water to below 10° and Eriochrome Black T is added in such an amount as to impart on shaking the first perceptible blue colour to the solution. The flask is removed from ice-water and titrated from a burette with 0·05*M* solution of zinc chloride until the colour turns red. Now 1 or 2 drops of 0·05*M* solution of EDTA are added just to get back the blue colour and then the solution is titrated with 0·01*M* solution of zinc chloride until a bluish-violet end-point is obtained. The colour should persist for one minute while the solution is cooled in ice-water during standing. 1·5 g of sodium fluoride are now added, the solution is heated to near boiling (the boiling temperature of the solution is around 80°) and let stand on the hot plate for 20 minutes so as to keep it near the boiling point. The solution is then cooled to below 10° and titrated with 0·01*M* solution of zinc chloride to a persistent bluish-violet colour. The time required for one determination is 60 minutes approximately.

Calculation of the results

$$A = n \times f \times 0{\cdot}2697$$

where: A = mg Al found.
n = ml 0·01*M* solution of zinc chloride.
f = the factor of the zinc chloride solution.
0·2697 = the factor for aluminium.

Tables IV, V and VI show some typical results obtained, according to this method, for aluminium alone and for aluminium in the presence of iron, copper and phosphate.

TABLE IV. DETERMINATION OF ALUMINIUM WITH EDTA, WHEN PRESENT ALONE

Exp. No.	Al present *mg*	Al found *mg*	Difference *mg*	Relative error %
1	0·4513	0·4540	+0·0027	+0·6
2	0·9026	0·8990	−0·0036	−0·4
3	2·256	2·255	−0·001	—
4	4·513	4·525	+0·012	+0·3
5	9·026	9·048	+0·022	+0·2

Conclusion

The results for aluminium alone are accurate, especially in the determination of more than one mg of aluminium. (Table IV.)

TABLE V. DETERMINATION OF ALUMINIUM WITH EDTA, IN THE PRESENCE OF IRON

Exp. No.	Fe^{3+} present *mg*	Al present *mg*	Al found *mg*	Difference *mg*	Relative error %
1	0·582	0·4513	0·4500	−0·0013	−0·3
2	4·656	0·4513	0·4550	+0·0037	+0·8
3	4·656	2·256	2·267	+0·011	+0·5
4	5·820	2·256	2·265	+0·009	+0·4
5	4·656	4·513	4·527	+0·014	+0·3
6	5·820	4·513	4·501	−0·012	−0·3
7	4·656	9·026	9·048	+0·022	+0·2
8	5·820	9·026	9·024	−0·002	—

The determination of aluminium in the presence of iron is accurate. (Table V.)

Notes: 1. More than 5 mg of iron make the titration difficult due to the yellow colour of iron chelate and also to the effect of iron on the indicator. For example, various shades of olive-green to green were obtained which made the titration of EDTA with the zinc chloride solution difficult.

TABLE VI. DETERMINATION OF ALUMINIUM WITH EDTA IN THE PRESENCE OF COPPER

Exp. No.	Cu^{2+} present *mg*	Al present *mg*	Al found *mg*	Difference *mg*	Relative error %
1	0·500	0·4513	0·4527	+0·0014	+0·3
2	4·000	0·4513	0·4555	+0·0042	+0·9
3	3·000	2·256	2·242	−0·014	−0·6
4	4·000	2·256	2·270	+0·014	+0·6
5	3·000	4·513	4·526	+0·013	+0·3
6	4·000	4·513	4·527	+0·014	+0·3
7	3·000	9·026	9·007	−0·019	−0·2
8	4·000	9·026	9·053	+0·027	+0·3

2. Iron was added as a solution of ferric chloride acidified with hydrochloric acid 5%.

The determination of aluminium in the presence of copper is accurate. (Table VI).

Notes: 1. More than 4 mg of copper make the titration difficult due to the blue colour of copper chelate and also to the effect of copper on the indicator.

2. Copper was added as a solution of copper nitrate acidified with nitric acid 1%.

TABLE VII. DETERMINATION OF ALUMINIUM WITH EDTA IN THE PRESENCE OF PHOSPHATE

Exp. No.	P_2O_5 present *mg*	Al present *mg*	Al found *mg*	Difference *mg*	Relative error %
1	20	0·4513	0·4540	+0·0027	+0·6
2	50	0·4513	0·4558	+0·0045	+1·0
3	20	2·256	2·249	−0·007	−0·3
4	50	2·256	2·265	+0·009	+0·4
5	20	4·513	4·525	+0·012	+0·3
6	50	4·513	4·527	+0·014	+0·3
7	20	9·026	9·048	+0·022	+0·2
8	50	9·026	9·007	−0·019	−0·2

The determination of aluminium in the presence of phosphate is accurate. (Table VII.)

Notes: 1. Phosphate does not interfere in the determination of aluminium, provided only 1–2 drops of 0·05*M* solution of zinc chloride are added in excess during the titration of the excess EDTA. When more than a few drops of the zinc chloride solution are added, zinc phosphate may precipitate, which impairs the sharpness of the end-point.

2. Phosphate was added in the form of potassium dihydrogen phosphate and calculated as P_2O_5.

Discussion

(1) *Acidity of sample:* The solution of the sample should not contain excessive amounts of free acids (*e.g.* not more than 5 ml conc. HCl). Free acids give rise to an equivalent amount of ammonium salts during the ammonia-neutralisation step. These salts, being a buffer on the acidic side of the pH scale, counteract the buffer action of ammonium acetate and impair the sharpness of the Eriochrome end-point. Table VIII shows the effect of the pH on the accuracy of the aluminium determination and the sharpness of the end-point.

TABLE VIII. EFFECT OF pH ON THE ACCURACY OF THE ALUMINIUM DETERMINATION AND ON THE SHARPNESS OF THE END-POINT

Exp. No.	Al present *mg*	Al found *mg*	Difference *mg*	Rel. error %	pH	Notes
1	4·513	4·500	−0·013	−0·3	6·0	end-point not sharp
2	4·513	4·519	+0·006	+0·1	6·7	end-point sharp
3	4·513	4·524	+0·011	+0·2	7·0	end-point sharp
4	4·513	4·527	+0·014	+0·3	7·3	end-point sharp
5	4·513	4·420	−0·093	−2	8·0	end-point sharp

Conclusion: The pH has no effect on the accuracy of the aluminium determination within the range 6·7–7·3.

(2) *Heating period with sodium fluoride:* The solution should be heated with 1·5 g of sodium fluoride for 20 minutes in order to liberate the EDTA quantitatively from the aluminium chelate at

pH 6·7–7·3. Table IX indicates the effect of the heating period and of the amount of sodium fluoride on the accuracy of the determination.

TABLE IX. EFFECT OF HEATING PERIOD AND AMOUNT OF SODIUM FLUORIDE ON THE ACCURACY OF THE ALUMINIUM DETERMINATION

Exp. No.	Heating period *minutes*	Sodium fluoride added *g*	Al present *mg*	Al found *mg*	Difference *mg*	Rel. error %
1	5	1·5	4·513	4·462	−0·051	−1·1
2	10	1·5	4·513	4·490	−0·023	−0·5
3	20	0·5	4·513	4·422	−0·091	−2·0
4	20	1·0	4·513	4·494	−0·019	−0·4
5	20	1·5	4·513	4·522	+0·009	+0·2
6	10	1·5	9·026	8·986	−0·040	−0·4
7	20	0·5	9·026	8·901	−0·125	−1·4
8	20	1·5	9·026	9·032	+0·006	+0·1

In the Schwarzenbach table for the log of the formation constants of chelates of metals with EDTA,[23] ferric and cupric ions precede aluminium. This indicates that the two former ions are chelated before aluminium when excess EDTA is introduced into a solution of these three ions. Therefore, the back-titration method for the determination of aluminium—according to procedure "A"—is not applicable in the presence of iron and copper. In such a case the fluoride method, *i.e.* procedure "B" for the determination of aluminium by an indirect method, is applicable.

PART III: THE DEVELOPMENT OF A CATION-EXCHANGE METHOD FOR THE DETERMINATION OF ALUMINIUM IN THE PRESENCE OF TITANIUM, MANGANESE, CALCIUM AND MAGNESIUM

The interference of titanium, manganese, calcium and magnesium in the determination of aluminium

We found that titanium, manganese, calcium and magnesium seriously interfere with the determination of aluminium, according to the procedure given in Part II. This interference is due to the fact that at pH 6·7–7·3 these cations are partially chelated by EDTA giving rise to an equilibrium condition:

$$\text{metal ion} + \text{free EDTA} \rightleftharpoons \text{metal chelate}$$

This equilibrium condition exists when the excess of EDTA is titrated with zinc chloride solution, whereas the metal chelate does not dissociate completely, and hence the indistinct end-point. At the stage where sodium fluoride is added and the solution is heated to liberate EDTA from the aluminium chelate, metal fluorides are obtained and free EDTA is liberated giving rise to high results for aluminium:

$$\text{EDTA-chelate} + \text{NaF} \rightarrow \text{cation fluoride} + \text{EDTA-Na}$$

The interference of manganese, titanium, calcium and magnesium was observed when the excess EDTA, added to the solution containing aluminium plus one of these cations, was titrated with zinc solution. The end-point was not sharp and the bluish-violet colour turned blue within a few seconds. The return of the colour was due to the dissociation of the metal chelate when nearing the end-point, as the excess of free EDTA was removed during the titration with zinc chloride solution.

Several known complexing agents were tried in order to mask these interfering cations, but without success. An attempt was made to eliminate these cations with the aid of a cation-exchange resin, and three resins were systematically studied for this purpose: Amberlite IR-100, Amberlite IR-120 and Dowex-50. Their behaviour towards free EDTA and aluminium chelate was investigated. The results are given in tables X, XI and XII.

TABLE X. THE BEHAVIOUR OF FREE EDTA TOWARDS SOME CATION-EXCHANGE RESINS

Exp. No.	Type of resin	Cycle form	0·01*M* EDTA passed through the resin *ml*	0·01*M* EDTA found in the effluent *ml*	pH of the effluent
1	Amberlite IR-100	H	25	0·5	2·2
2	Amberlite IR-120	H	25	2·1	2·5
3	Dowex-50	H	25	0·7	2·3
4	Amberlite IR-100	Na	25	24·5	7·4
5	Amberlite IR-120	Na	25	24·6	7·5
6	Dowex-50	Na	25	24·6	7·5
7	Amberlite-IR-100	NH_4	25	24·6	5·7
8	Amberlite IR-120	NH_4	25	24·6	5·5
9	Dowex-50	NH_4	25	24·2	5·6

CONCLUSIONS

1. The resins in the hydrogen cycle cannot be used for two reasons: (*a*) They retain free EDTA (Exp. 1, 2, 3), (*b*) Free acids are liberated during the ion exchange and the consequent lowering of pH interferes with the determination of aluminium. (Table X.)

2. In comparison with the acid cycle, the retention of EDTA by the resins in the sodium or ammonium cycle is very low. (Table X.)

TABLE XI. THE BEHAVIOUR OF Al-EDTA TOWARDS CATION-EXCHANGE RESINS

Exp. No.	Type of resin	Cycle form	Al present *mg*	Al found *mg*	Difference *mg*	Rel. error %	pH of the effluent
1	Amberlite IR-100	H	4·513	2·360	2·153	−47	less than 1
2	Amberlite IR-120	H	4·513	2·200	2·313	−51	less than 1
3	Dowex-50	H	4·513	2·592	1·921	−43	less than 1

The resins in the hydrogen cycle retain Al-EDTA. (Table XI.)

Note: The aluminium was determined in the effluent according to the procedure given in Part II.

Since free EDTA is not retained by the resins in the sodium or ammonium cycle, our next step was to find out the behaviour of Al-EDTA towards these resins. This was tried as follows: known amounts of aluminium were treated with excess EDTA. After adjusting the pH with ammonia to the yellow colour of methyl orange, the solution was boiled for three minutes, cooled and passed through the resin. Aluminium was determined in the effluent after concentration to about 20–30 ml, following the procedure given in Part II. The results are given in Table XII.

Conclusion

Al-EDTA passes quantitatively through the cation-exchange resins in the cycle-form sodium or ammonium (Table XII).

Taking into account the presence of manganese, titanium, calcium and magnesium in the sample to be analysed, the procedure to be followed for the determination of aluminium in the presence of these cations should be to add EDTA in slight excess to that required for aluminium only and to pass the solution through resin. These interfering cations are retained, while Al-EDTA passes through into the effluent.

TABLE XII. THE BEHAVIOUR OF Al-EDTA TOWARDS CATION-EXCHANGE RESINS IN THE CYCLE FORM SODIUM OR AMMONIUM

Exp. No.	Type of resin	Cycle form	Al present *mg*	Al found *mg*	Difference *mg*	Relative error %
1	Amberlite IR-100	Na	0·4513	0·4527	+0·0014	+0·3
2	Amberlite IR-100	Na	2·256	2·265	+0·009	+0·4
3	Amberlite IR-100	Na	4·513	4·526	+0·013	+0·3
4	Amberlite IR-100	NH_4	2·256	2·249	−0·007	−0·3
5	Amberlite IR-100	NH_4	4·513	4·526	+0·013	+0·3
6	Amberlite IR-120	Na	2·256	2·242	−0·014	−0·6
7	Amberlite IR-120	Na	4·513	4·526	+0·013	+0·3
8	Amberlite IR-120	NH_4	2·256	2·270	+0·014	+0·6
9	Amberlite IR-120	NH_4	4·513	4·526	+0·013	+0·3
10	Dowex-50	Na	2·256	2·267	+0·011	+0·5
11	Dowex-50	Na	4·513	4·526	+0·013	+0·3
12	Dowex-50	NH_4	2·256	2·267	+0·011	+0·5
13	Dowex-50	NH_4	4·513	4·501	−0·012	−0·3

It was found essential not to add a large excess of EDTA over that required to chelate aluminium; otherwise the interfering cations—manganese, calcium, titanium and magnesium—will pass through into the effluent. This is due to the fact that the degree of dissociation of the chelates of these metals is higher in the absence of a large excess of free EDTA and as a result, the cations of the interfering metals are exchanged by the sodium or ammonium ions from the resin.

A spot test was then devised for the detection of a slight excess of free EDTA, which is a modification of the spot test described by Feigl[24] for the detection of zinc with dithizone.

Spot test for free EDTA

This test must indicate the presence of free EDTA at the point where enough has been added to chelate only aluminium, copper and iron in the presence of the above mentioned cations. The pH at which this test should be performed must not exceed 4, since manganese, calcium, magnesium and titanium are appreciably chelated above this pH value.

According to Feigl,[24] the spot test for the detection of zinc is performed by mixing in a small test tube a drop of the solution to be tested with a drop of dithizone solution in carbon tetrachloride. In the presence of zinc the green colour of dithizone turns red due to the formation of zinc dithizonate chelate.

The mechanism of our spot test reaction for EDTA is as follows: a drop of the solution to be tested is mixed on a spot plate with zinc dithizonate solution (red) at pH 3·4–4·0. If free EDTA is present, the colour turns green owing to the dithizone liberated from the zinc dithizonate. The zinc dithizonate solution is composed of a buffer of pH 2·6 (HCl plus potassium biphthalate)—according to Tomiček[25]—to which traces of zinc and a certain amount of acetone and carbon tetrachloride are added. The use of carbon tetrachloride only as a solvent for dithizone does not permit enough contact between the aqueous solution to be tested and the carbon tetrachloride solution of dithizone, thus the addition of acetone is necessary. The pH of the buffer is raised to 3·8 after the addition of the organic solvents. It was found that dithizone functions well at this pH and 0·5 μg of free EDTA can be detected in one drop of the solution to be tested. It was also found that the presence of carbon tetrachloride increases the sensitivity of the test. Since solutions of dithizone are unstable at room temperature, dithizone can be added to the buffer when the spot test is to be performed. As its concentration in the buffer is low (0·005 %) dithizone is added to the buffer after being mixed with solid sodium chloride (1 % mixture).

Copper interferes with the spot test for EDTA. Since copper dithizonate is more stable than copper-EDTA, dithizone will chelate copper and thus free EDTA cannot be indicated in the presence of copper; colour change to green could not be observed. It was observed, however, that the incorporation of a little sodium diethyldithiocarbamate in the dithizone-sodium chloride mixture, which is added to the buffer solution, will obviate this difficulty. Copper will form a chelate with the carbamate which is more stable than the copper dithizonate. Thus the interference of copper in the spot test for free EDTA is eliminated.

The cation-exchange resin used

Since the pH of the effluent for the resin in the ammonium form is lower than that in the sodium form (Table X, Exps. 4–9) the former is more suitable. This is because the dissociation of manganese-, titanium-, calcium- or magnesium-EDTA is higher at lower pH values and these cations are more completely eliminated by the resin. Amberlite IR-120 was used in all subsequent experiments.

PART IV: THE DETERMINATION OF ALUMINIUM IN THE PRESENCE OF IRON, COPPER, MANGANESE, TITANIUM, CALCIUM, MAGNESIUM AND PHOSPHATE

Reagents and standard solutions

1. *0·05M solution of Complexone-III (EDTA):* prepared by dissolving 18·610 g of Complexone-III in 0·1*N* solution of NaOH and making the total volume up to one litre with 0·1*N* NaOH.

2. *0·01M solution of Complexone-III (EDTA):* (See Part I, reagent No. 2).

3. *Spot test buffer solution:* prepared by mixing 33 ml of 0·2*M* HCl with 50 ml of 0·2*M* potassium biphthalate followed by the addition of 100 ml of acetone, 3 ml of carbon tetrachloride and 0·5 ml of 0·01*M* solution of zinc chloride.

4. *Dithizone indicator:* 0·1 g dithizone and 0·1 g sodium diethyldithiocarbamate are intimately ground together in a mortar with 10 g of sodium chloride.

5. *Ammonium chloride solution:* 15%.

6. *Cation-exchange resin:* Amberlite IR-120 was used in a column 30 cm long and 2 cm in diameter. The resin was regenerated by passing through about 300 ml of ammonium chloride solution 15% at a flow rate of 10 ml per minute, followed by washing with equal volume of water at a flow rate of 40 ml per minute. The regeneration is done after passing through solutions of samples ten times.

7. *Ammonia solution:* 1%.

8. *Ammonia solution:* 5%.

9. *Methyl orange indicator:* 0·05% solution in water.

10. *Isopropanol:* The reagent should be tested before use as follows: 100 ml of water, 35 ml of the *iso*propanol, 10 ml ammonium acetate 10%, 1 ml triethanolamine 10% and Eriochrome Black T indicator are introduced into a 250-ml Erlenmeyer flask. The solution is titrated with 0·01*M* solution of EDTA to a blue end-point and then titrated with 0·01*M* solution of zinc sulphate to a bluish-violet colour. The colour change in these two titrations should be sharp and easily seen with one drop of titrant.

11. *Ammonium acetate solution:* 10%.

12. *Eriochrome Black T indicator:* (See Part I, reagent No. 4).

13. *Sodium fluoride.*

14. *Triethanolamine:* 10%.

15. *0·01M solution of zinc sulphate:* prepared by dissolving 2·875 g of zinc sulphate ($ZnSO_4 . 7H_2O$) in distilled water, and making up the total volume to one litre after the addition of one drop of concentrated HCl. The solution is standardised as follows: 25 ml of 0·01*M* solution of EDTA are introduced into a Pyrex 250-ml Erlenmeyer flask, 80–100 ml of distilled water are added, followed by 10 ml ammonium acetate solution 10%, 25 ml *iso*propanol, 1 ml triethanolamine 10% and Eriochrome Black T indicator. The solution is now titrated from a burette with the zinc sulphate solution till the colour turns bluish-violet.

16. *Hydrochloric acid:* 0·1*N*.

Procedure for the determination of aluminium in the presence of iron, copper, titanium, manganese calcium, magnesium and phosphate

The solution of the sample, containing 5–15 mg of aluminium, is introduced into a Pyrex 150-ml beaker. Water is added to a total volume of about 15 ml, followed by one drop of methyl orange indicator. The solution is neutralised with ammonia 5% till it turns yellow. 4 Ml of $0{\cdot}1N$ HCl are then added, the solution is heated to near boiling, and 0·4 ml portions of $0{\cdot}05M$ EDTA are introduced until enough has been added to chelate the aluminium, iron and copper in the sample.* When approaching approximately the point of chelating Al, Fe, Cu in the sample with EDTA, the solution is tested for the presence of free EDTA as follows: 5 ml of the spot test buffer solution (Reagent No. 3) are introduced into a test tube and about 15 mg of the dithizone-carbamate-NaCl indicator mixture (Reagent No. 4) are added and dissolved. The solution thus obtained is stable for about one hour. 5–6 Drops of the spot solution are introduced into a spot plate and the tip of a glass rod moistened with the solution of the analysed sample is brought in contact with the spot solution and stirred. If the red colour does not turn green, the addition of 0·4 ml portions of $0{\cdot}05M$ EDTA to the solution of the sample is continued with the application of the spot test till the colour of the spot solution turns green, indicating excess free EDTA. A large excess of the latter should be avoided. It was found essential to apply the spot test while the solution of the analysed sample is kept nearly boiling. The beaker is now covered with a watch-glass and the solution is boiled gently for three minutes. It is then left to cool to room temperature and ammonia solution 1% is added dropwise until the colour of the solution turns yellow. The addition of excess ammonia should be avoided. 2 Ml of $0{\cdot}01M$ solution of zinc sulphate are now added, followed by $0{\cdot}1N$ HCl, until the colour of the solution turns orange, but not red. The solution is then passed through a column containing Amberlite IR-120 in the ammonium cycle at a flow rate of about 8 ml per minute. The resin is washed with distilled water until the total volume of the effluent amounts to 200–230 ml. The effluent is received into a Pyrex 500-ml Erlenmeyer flask and to it are then added 75 ml *iso*propanol, 10 ml ammonium acetate solution 10% and 1 ml triethanolamine 10%. After cooling below 10°, a little Eriochrome Black T indicator is added and the excess of EDTA is titrated with $0{\cdot}01M$ solution of zinc sulphate to a permanent bluish-violet end-point. 1·5 G of sodium fluoride are now added, the solution is heated to near boiling and then kept at this temperature for 20 minutes. After cooling again to below 10°, the solution is titrated with $0{\cdot}01M$ solution of zinc sulphate to a persistent bluish-violet end-point.

Calculation of the results

$$A = n \times f \times 0{\cdot}2697$$

where A = mg Al found
n = ml $0{\cdot}01M$ solution of zinc sulphate
f = factor of the zinc sulphate solution
0·2697 = the factor for aluminium

The time required for a single determination is 1½–1¾ hours approximately, whereas much less time is required when determinations are carried out in series.

The accuracy of the determination of aluminium in the presence of various anions

A series of determinations was done according to the procedure described above in order to test the accuracy of the method in the presence of various quantities of anions (NO_3^-, CH_3COO^-, SO_4^{2-}, Cl^-). Some of the typical results obtained are shown in Table XIII.

Conclusion

The determination of aluminium in the presence of chloride, sulphate, acetate and nitrate ions is accurate.

Table XIV shows some typical results obtained for aluminium in the presence of iron, copper, titanium, manganese, calcium, magnesium and phosphate.

Conclusions

(1) The method described for the determination of aluminium is accurate.

TABLE XIII. DETERMINATION OF ALUMINIUM WITH EDTA IN THE PRESENCE OF CHLORIDE, SULPHATE, ACETATE AND NITRATE

Exp. No.	Anion added	Compound form of anion added	Anion added *mg*	Al present *mg*	Al found *mg*	Difference *mg*	Relative error %
1	Chloride	NH_4Cl	1100	9·026	9·053	+0·027	+0·3
2	Chloride	NH_4Cl	1100	13·539	13·550	+0·011	+0·1
3	Sulphate	$(NH_4)_2SO_4$	500	9·026	9·007	−0·019	−0·2
4	Acetate	CH_3COONa	800	9·026	9·007	−0·019	−0·2
5	Nitrate	NH_4NO_3	1000	9·026	9·007	−0·019	−0·2
6	Nitrate	NH_4NO_3	1100	13·539	13·536	−0·003	—

* In order to determine the approximate volume of 0·05*M* EDTA solution necessary and also to avoid random trials, a preliminary test with the same aliquot of the solution of the sample is done, adding larger portions (2 ml) of 0·05*M* EDTA solution.

(2) The maximum limit allowable for other cations that may be present without affecting the accuracy of the determination of aluminium is as follows :

Iron	8 mg
Copper	3 mg
Titanium	1 mg
Manganese	20 mg
Calcium	20 mg
Magnesium	20 mg
Phosphate (as P_2O_5)	40 mg

Note: Since the titration is performed in a relatively large volume, the tolerance for iron is increased above the 5-mg limit mentioned in Part II of this paper.

DISCUSSION

1. As previously pointed out, the solution of the sample should be weakly acidic. The analysed solution is, therefore, neutralised with ammonia and re-acidified with a limited amount of hydrochloric acid to a pH below 2. Excessive amounts of free acids interfere, for example more than 5 ml of concentrated hydrochloric acid in the sample taken. In such cases the solution should be concentrated to a total volume of about 0·5 ml before analysis.

2. Reducing agents interfere, if the sample contains iron or copper, and should be previously oxidised with an excess of bromine water. The excess of the latter should be expelled by boiling for several minutes; thus iron and copper exist in their higher valency states.

3. Oxalates, tartrates, citrates, pyrophosphates and fluorides interfere, and they should be previously eliminated by evaporation with 0·2 ml of concentrated sulphuric acid.

4. As already pointed out, it is necessary to boil the solution with the excess of EDTA in order to stabilise the aluminium chelate. It was found that the aluminium can be also stabilised by boiling the weakly acid solution with excess of EDTA instead of doing so after neutralisation with ammonia, *i.e.* instead of boiling the neutral solution.

TABLE XIV. DETERMINATION OF ALUMINIUM IN THE PRESENCE OF IRON, COPPER, TITANIUM, CALCIUM, MAGNESIUM AND PHOSPHATE

Exp. No.	Compound form of cation added *mg*	Cation added *mg*	Al present *mg*	Al found *mg*	Diff. *mg*	Rel. error %
1	$FeCl_3$	Fe 8	4·513	4·526	+0·013	+0·3
2	$FeCl_3$	Fe 8	13·539	13·511	−0·028	−0·2
3	$Cu(NO_3)_2$	Cu 3	9·026	9·075	+0·049	+0·5
4	$Cu(NO_3)_2$	Cu 3	13·539	13·500	−0·039	−0·3
5	$FeCl_3$, $Cu(NO_3)_2$, KH_2PO_4	Fe 8, Cu 3, P_2O_5 40	4·513	4·490	−0·023	−0·5
6	$FeCl_3$, $Cu(NO_3)_2$, KH_2PO_4	Fe 8, Cu 3, P_2O_5 40	13·539	13·580	+0·041	+0·3
7	$Ti(SO_4)_2$	Ti 1	9·026	9·075	+0·049	+0·5
8	$Ti(SO_4)_2$	Ti 1	13·539	13·550	+0·011	+0·1
9	$Ti(SO_4)_2$, $FeCl_3$, KH_2PO_4	Ti 1, Fe 8, P_2O_5 40	4·513	4·553	+0·040	+0·9
10	$Ti(SO_4)_2$, $FeCl_3$, KH_2PO_4	Ti 1, Fe 8, P_2O_5 40	9·026	9·048	+0·022	+0·2
11	$MnSO_4$	Mn 20	4·513	4·526	+0·013	+0·3
12	$MnSO_4$	Mn 20	13·539	13·536	−0·003	—
13	$MnSO_4$, $FeCl_3$, KH_2PO_4	Mn 20, Fe 8, P_2O_5 40	4·513	4·494	−0·019	−0·4
14	$MnSO_4$, $FeCl_3$, KH_2PO_4	Mn 20, Fe 8, P_2O_5 40	13·539	13·587	+0·048	+0·4
15	$CaCl_2$	Ca 20	4·513	4·526	+0·013	+0·3
16	$CaCl_2$	Ca 20	13·539	13·500	−0·039	−0·3
17	$MgSO_4$	Mg 20	4·513	4·490	−0·023	−0·5
18	$MgSO_4$	Mg 20	13·539	13·587	+0·048	+0·4
19	$CaCl_2$, $MgCl_2$	Ca 20, Mg 20	4·513	4·494	−0·019	−0·4
20	$CaCl_2$, $MgCl_2$	Ca 20, Mg 20	13·539	13·550	+0·011	+0·1
21	$CaCl_2$, $MgCl_2$, KH_2PO_4	Ca 20, Mg 20, P_2O_5 40	4·513	4·526	+0·013	+0·3
22	$CaCl_2$, $MgCl_2$, KH_2PO_4	Ca 20, Mg 20, P_2O_5 40	13·539	13·580	+0·041	+0·3
23	$CaCl_2$, $MgCl_2$, $FeCl_3$	Ca 20, Mg 20, Fe 8	4·513	4·494	−0·019	−0·4
24	$CaCl_2$, $MgCl_2$, $FeCl_3$	Ca 20, Mg 20, Fe 8	13·539	13·500	−0·039	−0·3
25	$CaCl_2$, $MgCl_2$, $Cu(NO_3)_2$	Ca 20, Mg 20, Cu 2	9·026	9·007	−0·019	−0·2
26	$CaCl_2$, $MgCl_2$, $Cu(NO_3)_2$	Ca 20, Mg 20, Cu 2	13·539	13·538	−0·001	—
27	$FeCl_3$, $Cu(NO_3)_2$, KH_2PO_4, $Ti(SO_4)_2$, $CaCl_2$, $MgCl_2$, $MnSO_4$	Fe 8, Cu 3, P_2O_5 40, Ti 1, Mn 20, Ca 20, Mg 20	4·513	4·494	−0·019	−0·4
28	$FeCl_3$, $Cu(NO_3)_2$, KH_2PO_4, $Ti(SO_4)_2$, $CaCl_2$, $MgCl_2$, $MnSO_4$	Fe 8, Cu 3, P_2O_5 40, Ti 1, Mn 20, Ca 20, Mg 20	13·539	13·587	+0·048	+0·4

5. It was found, at this stage, that by adding triethanolamine to the solution before the titration of the excess EDTA, it was no longer necessary to evaporate the solution to a small volume in order to maintain a 40% concentration of *iso*propanol and prevent the partial interference of iron and copper with the colour change of the indicator.

6. Through the addition of a small fixed amount of 0·01*M* solution of zinc (2 ml) the quantity of excess EDTA present can be reduced to the minimum since it is chelated by zinc. Thus larger amounts of foreign cations can be tolerated, because the dissociation of the chelates of these cations is more complete owing to the reduction of the quantity of excess EDTA.

7. Instead of zinc chloride solution as titrant, 0·01*M* solution of zinc sulphate can be used.

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Zusammenfassung—Die Verfasser haben eine schnelle und exakte volumetrische Methode zur Bestimmung des Aluminiums (5–15 mg) mit Komplexon-III in Anwesenheit von Eisen, Kupfer, Titan, Mangan, Calcium, Magnesium und Phosphat ausgearbeitet.

Résumé—Les auteurs ont élaboré une méthode volumétrique rapide et exacte pour la détermination de l'aluminium (5–15 mg) au moyen de Complexone-III en présence de Fer, Cuivre, Titane, Manganèse, Calcium, Magnésium et Phosphate.

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THE SEPARATION AND DETERMINATION OF NIOBIUM AND TANTALUM BY PARTITION CHROMATOGRAPHY

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Summary—A procedure is outlined for the separation and determination of niobium and tantalum by paper chromatography. A mixture of methyl *iso*butyl ketone and hydrofluoric acid was used as solvent and the metals were detected by means of 8-hydroxyquinoline. The minimum amount of each element detectable is 20 μg.

The procedure was applied successfully to the quantitative determination of small amounts of niobium and tantalum in a steel.

BECAUSE of the lanthanide contraction the atomic volumes of niobium and tantalum are almost identical, and the chemical resemblance between them is very close. Both elements are invariably associated together in minerals, and are occasionally encountered in steels and other alloys. The great difficulties in the analysis of these metals are stressed by at least two authors.[1,2] Discussing the importance of niobium as a metal in nuclear technology, Colter[3] states that, although there are a number of methods used for the extraction of niobium from columbite, the major difficulty in all of them is separation from the accompanying tantalum.

It is not surprising that, because of the difficulty in separating these elements, many attempts have been made to determine one element in the presence of the other.[4–6]

An extensive review of recent works on the separation of these two elements by means of organic solvents has been prepared by West.[7] A feature of many of these separations based on liquid-liquid extraction processes is, however, that while they are successful for microgram amounts of the elements, they are not at all efficient when the quantities are increased.

Few chromatographic methods have been developed for the separation of the elements. Cabell and Milner[8] achieved a separation using anion-exchange resin De-Acidite FF. The separation is claimed to be quantitative, less than 0·01% of tantalum being present in the niobium fraction. Bruninx *et al.*, report the separation of these elements on paper by electrophoresis.[9] The largest quantities separated are 50 μg. The same authors also[10] report a separation by paper chromatography using the oxalates of the metals and a solvent-mixture composed of ethyl methyl ketone and 10*N* hydrochloric acid. Microgram amounts are separated.

This paper describes the separation and determination of the elements niobium and tantalum by means of partition chromatography.

EXPERIMENTAL

Preliminary investigations

Little information is available to indicate the effect of simple alcohols or mixtures of alcohols on niobium and tantalum. A number of experiments were therefore carried out on Whatman No. 1 filter paper using methanol, ethanol and butanol. These alcohols or mixtures of alcohols gave no separation. Ketones were next used and they showed some separation. With methyl propyl ketone, niobium remained at the top of the paper and tantalum moved with the solvent-front but showed considerable "tailing". Methyl *iso*butyl ketone gave a similar result to methyl propyl ketone while mesityl oxide, *iso*phorone and diacetyl alcohol showed little improvement.

Admixture of alcohols with the ketones only succeeded in destroying the partial separation achieved by ketones alone.

Simple acids were now tried and it was found that hydrofluoric acid effected a separation. The positions of the niobium and tantalum on the paper were, however, reversed.

The behaviour of acid-ketone mixtures was now examined. Since the metals were present as their fluorides, hydrofluoric acid was used. This showed a marked improvement on the ketone separation in all cases. It therefore appeared necessary to examine the composition of the acid-ketone mixtures thoroughly in order to find that best suited to the separation. Two solvent-mixtures showed promise, methyl propyl ketone and methyl *iso*butyl ketone, each with hydrofluoric acid. These were examined in detail, and some of the results are shown in Table I.

TABLE I

No.	Solvent mixture	R_f values	
		Nb	Ta
1*	MPK 48 ml : HF 2 ml 2%	0–0·20	0·83–0·95
2*	MPK 46 ml : HF 2 ml 2%	0·40	0·90
3	M*iso*BK 50 ml : HF 2½ ml 4%	0·60	0·89
4*	M*iso*BK 50 ml : HF 1½ ml 40%	0·1	0·87
5*	M*iso*BK 50 ml : HF 3 ml 4%	0·70	0·80
6	M*iso*BK 50 ml : HF 2 ml 4%	0·53	0·63
7	M*iso*BK 50 ml : HF 2½ ml 2%	0·23	0·72
8	M*iso*BK 50 ml : HF 2 ml 40%	0·80	0·91
9*	M*iso*BK 50 ml : HF 2 ml 20%	0·15–0·40	0·84
10*	M*iso*BK 50 ml : HF 4 ml 4%	0·43	0·81

*Indicates "bearding" and/or "tailing" with the solvent mixture.

Mixtures of methyl propyl ketone and acid were not entirely satisfactory because of the "tailing" which occurred. Of the methyl *iso*butyl ketone-hydrofluoric acid mixtures, the best separation and banding were obtained with solvent-mixture No. 3, containing 2·5 ml of 4% hydrofluoric acid in 50 ml of ketone. This is a two-phase system, and is used directly on preparation. The niobium in this two-phase solvent mixture moves with the acid front, and the tantalum with the ketone front. In approximately three hours the acid front travels 10 cm, and the ketone front 3 cm further. This gives an excellent separation of the two elements.

Spraying reagents

Most workers who have carried out investigations on niobium and tantalum have precipitated them by forming the thiocyanate complex,[11] the cupferron complex[12] or by the addition of pyrogallol.[13] Niobium has also been detected by tannic acid.[14]

All of these reagents were found to be unsatisfactory for development of the elements on a paper chromatogram, with the exception of tannic acid which, however, could only be used for niobium. It was considered, therefore, that it would be a great advantage if a single reagent could be found which would detect both elements on the chromatogram.

Various reagents were investigated but that which fulfilled requirements most satisfactorily was 8-hydroxyquinoline. A 5% (w/v) solution of the reagent in methanol–chloroform–water (48 : 48 : 4) was used.

Development of the bands may be carried out in two ways. Firstly, the paper may be sprayed with a 5*N* ammonium hydroxide solution and then with the 8-hydroxyquinoline solution. It is then dried in an oven at 120° and, as the strip dries, both metals develop as bright yellow bands. On the other hand, if the strip is not so sprayed with ammonium hydroxide solution, niobium may be detected as a bright orange and tantalum as a pale orange band. Under ultra-violet light niobium fluoresces bright yellow but tantalum, although visible, fluoresces only slightly. Although both methods are quite satisfactory, the limit of detection being the same in each case, the first procedure was used in all succeeding work.

DETAILED PROCEDURE

1. Place the solvent-mixture (methyl *iso*butyl ketone–4% HF) in the solvent trough of a Chromatank at least one hour before starting the experiment.
2. Cut sheets of Whatman No. 1 paper into strips 16 cm wide.
3. At distances of 2·5, 4 and 6 cm from the top, rule lines across the paper and bend along the first of these lines.
4. Along the 6-cm line place 0·01 ml of the metal fluorides. The spots should not be allowed to dry before inserting into the Chromatank.
5. Allow the solvent-mixture to run down the paper—the acid front to the 10-cm mark and the ketone to about the 15-cm mark. This development takes about three hours.
6. Remove the strips from the tank and allow to dry in air. The paper is now ready for spraying.
7. Attach the strip to the strip-holder and spray with 5*N* ammonium hydroxide solution and then with a 5% solution of 8-hydroxyquinoline in methanol-chloroform–water (48 : 48 : 4).
8. Dry the strip in an oven at 120° for 30 minutes.
9. Wash with hot water to remove excess 8-hydroxyquinoline.
10. Dry in an oven for about 1 hour.
11. Examine the strip in ultra-violet light when niobium will be observed as a brilliant yellow band (R_f 0·60). Tantalum, detected by the naked eye, has an R_f value of 0·90.

Standards, limits of detection, synthetic mixtures.

Standards of 20, 100, 250, 350, and 500 μg amounts were prepared for each element. For both elements the limit of detection is 20 μg and an upper limit of at least 1 mg may be used. These standards were very satisfactory.

Synthetic mixtures of "unknown" composition were analysed by one of us (I.A.P.S.). Estimations were carried out by comparison of band intensities and areas with the set of standards. The results are shown in Table II. Where the actual amount present differs from that found, the former is written in parentheses.

TABLE II

No.	Nb, μg	Ta, μg
1	400 (500)	20 (25)
2	300 (350)	350
3	50 (25)	30 (25)
4	—	200 (250)
5	230 (250)	—
6	220 (200)	250
7	25	425 (400)
8	20	—
9	400 (425)	20 (25)
10	—	25 (20)

Application of the method to quantitative determinations.

The success achieved in the semi-quantitative analysis of these elements suggested that the separation might be applied quantitatively. Since the elements exist on the chromatograms as their oxinates, investigations were centred on the removal of these from the paper and their determination spectrophotometrically. Each element was investigated separately.

(*a*) *Niobium.* Using the procedure outlined for the detection of this element, it was found that precipitation of niobium oxinate on the paper was complete. After detection the square of paper containing the developed band was cut out. To remove the complex from the paper it was shaken in a separatory funnel with 10 ml of hot 2*N* hydrochloric acid. To extract niobium oxinate from the acid solution chloroform was used. pH conditions for the extraction were found to be critical. On the acid side, extraction is small but, as the pH is increased, extraction increases to a maximum in the range pH 8–9. Above this range it again decreases. pH 8·5 was used in all subsequent investigations.

After adjustment of the pH with ammonia, using indicator paper, the niobium oxinate solution was shaken with three 3-ml portions of chloroform; the combined extracts were dried over sodium sulphate and make up to the 10-ml mark in a calibrated flask. This solution, when examined spectrophotometrically, showed a strong maximum at 385 mμ.

(*b*) *Tantalum.* As was the case for niobium, the procedure used for the detection of the element ensured complete precipitation of tantalum oxinate on the paper. Hot 2*N* hydrochloric acid was again very suitable for removal of all the complex from the paper and extraction of this complex by chloroform was greatest in the range pH 9–11. A pH of 10·0 was used in all subsequent investigations.

Extraction was carried out in exactly the same manner as described for niobium oxinate and the extracts, when examined spectrophotometrically, showed strong maxima at 310 mμ and 390 mμ.

Since at wave lengths 385 mμ (niobium) and 390 mμ (tantalum) there is no interference from 8-hydroxyquinoline, these values were chosen respectively for spectrophotometric determination of the elements.

Solutions of both metal oxinates showed adherence to Beer' laws.

Alloy analysis

The analysis of a "straight N6 18/12" Stainless Steel, with certificate figures by the Bureau of Analysed Samples, Ltd., was carried out using this procedure.

The bulk components of the steel were removed as soluble perchlorates, the niobium and tantalum perchlorates were ignited to the oxides and were treated with hydrofluoric acid to give the fluorides.

Procedure

Place 1 g of the steel in a beaker and dissolve in 100 ml of a 1 : 1 (v/v) mixture of 37 % hydrochloric acid and 70 % nitric acid.

Treat the solution with 100 ml of 71 % perchloric acid, heat to boiling, and reflux for 30 minutes. Cool. Treat with 100 ml of water and 100 ml of saturated sulphurous acid. Heat to boiling and digest for two hours. After cooling, filter and wash the residue with 2 % hydrochloric acid. Ignite at dull red heat for about one hour. Convert the oxides to the fluorides with 40 per cent hydrofluoric acid and a few drops of concentrated nitric acid. Dissolve the fluorides in 1 ml of hydrofluoric acid.

Results

The solution obtained using the above procedure was applied in 0·05-ml amounts to the paper and chromatograms were prepared using the methyl *iso*butyl ketone-hydrofluoric acid solvent-mixture. Development of the niobium and tantalum positions was carried out with 8-hydroxyquinoline and the oxinates of the elements were extracted into chloroform in the manner already described.

From prepared calibration curves, in the range 0–500 μg of metal the amounts of niobium and tantalum in steel were found to be: Nb 0·69 % (present 0·67 %); Ta 0·05 % (present 0·04 %).

It is interesting to note that a semi-quantitative analysis carried out independently, in which the developed oxinates on the paper were compared directly with the sets of standards, gave values of 0·65 % and 0·04 % for niobium and tantalum respectively.

Zusammenfassung—Es wird ein Verfahren für die Trennung und Bestimmung von Niob und Tantal mittels Papierchromatographie angegeben. Als Lösungsmittel dient eine Mischung von Methyl*iso*butylketon und Fluorwasserstoffsäure. Die Identifizierung der Metalle erfolgt mit 8-Oxychinolin und besitzt eine Nachweisgrenze von 20 μg. Das Verfahren wurde mit Erfolg für die quantitative Bestimmung kleiner Mengen von Niob und Tantal in nichtrostendem Stahl angewandt.

Résumé—Description d'un procédé de séparation et de dosage du niobium et du tantale par chromatographie sur papier. Utilisant comme solvant une mélange: méthyl*iso*butylcetone–acids fluorhydrique, on a identifié les métaux à l'aide de la 8-hydroxyquinoleine. La quantité minimum décelable de chaque élément est 20 μg.

On a pu appliquer avec succès cette méthode à la détermination quantitative du niobium et du tantale dans un acier..

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NUCLEATION IN ANALYTICAL CHEMISTRY

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Summary—Precipitation involves two processes, nucleation and subsequent crystal growth. The nucleation process is of extreme importance in determining the number and size of the final crystalline particles. The significance of experimental studies of nucleation is discussed and the need for further research indicated.

IN analytical chemistry it is often desirable that a precipitate be produced in the form of relatively large crystals. Such a precipitate is not only more easily handled during subsequent operations but is less subject to contamination, because its surface area is smaller than that of a micro-crystalline or gelatinous precipitate. Empirical rules for the formation of macro-crystalline precipitates were formulated by von Weimarn.[22] Subsequent studies of the kinetics of precipitation and of crystal growth have generally confirmed and elucidated these rules.

Two distinct steps are involved in precipitation. The first, nucleation, is the formation within a supersaturated solution of the first particles of precipitate capable of spontaneous growth. In the second step these first particles, not observable by the naked eye, grow as ions are deposited on them from the solution. The number of particles is determined by the number of nuclei formed in the initial step, and hence so are both the rate of precipitation and the particle size of the precipitate.

In a solution, ions interact with each other to form relatively short-lived clusters. Nucleation is generally considered to occur by this mechanism, with ions or molecules associating in a series of step-wise equilibria to form clusters of various sizes, as follows:

$$\begin{gathered} X + X \rightleftharpoons X_2 \\ X_2 + X \rightleftharpoons X_3 \\ \vdots \\ X_{n-1} + X \rightleftharpoons X_n \\ X_n + X \rightarrow X_{n+1} \end{gathered}$$

All the clusters smaller than X_n are a part of the mother phase. The nucleus is X_n, and is the smallest cluster which can be considered to be solid phase. Clusters in general tend to dissociate rather than to grow because growth requires work to extend the interface between the cluster and the solution. Dissociation is opposed by the tendency of the supersaturated solution to deplete itself by deposition of ions onto the clusters. The nucleus, X_n, is in metastable equilibrium with the solution so that either dissociation or growth can proceed with a decrease in free energy. At a given supersaturation there is one particle size which is in metastable equilibrium; particles smaller than this disperse whereas larger particles grow. This is expressed in the Kelvin-Gibbs equation derived for the case of a spherical droplet of liquid in contact with its supersaturated vapour:

$$RT \ln P_r/P_0 = 2\sigma V/r,$$

where

P_r = the vapour pressure of a drop of radius r,
P_0 = the vapour pressure of the plane liquid surface,
σ = surface tension of the droplet,
V = molal volume of the liquid.

CURRENT THEORIES

Two theoretical approaches to nucleation have been proposed. The classical theory, as given by Volmer,[21] Becker and Doering,[1] and Frenkel,[9] uses the work of formation of the nucleus, obtained from the surface tension, as the activation energy in a kinetic expression for the nucleation rate. The size of the nucleus is obtained from the Kelvin equation or a modification of it, and consequently is a function of supersaturation. The rate of nucleation is found to increase very rapidly with increasing supersaturation, so that the formation of nuclei appears to be a critical function of the degree of supersaturation. The theory, derived for condensation of a vapour, has been modified for nucleation in condensed systems by Turnbull and Fisher.[20] Turnbull[19] gives the following, for nucleation of $BaSO_4$:

$$I \approx K_V \exp\left[-a\sigma^3 v^2/k^3T^3(\ln S)^2\right],$$

where

I = rate of nucleation,
$K_V \approx n\nu \exp\left[-\Delta G_A/kT\right]$,
a is a geometrical factor,
σ = interfacial energy per area between nucleus and solution,
v = volume per "molecule" of $BaSO_4$ crystal,
S = critical supersaturation = $(K_{\text{I.P.}}/K_{\text{S.P.}})^{1/2}$, where $K_{\text{I.P.}}$ is the ion-product,
n = number of Ba^{2+} and SO_4^{2-} ions per volume,
ν = jump frequency,
ΔG_A = free energy of activation for growth of crystals.

This equation is difficult to apply because the energy terms are not well defined. For example, there are little available data on the surface energy of solids; further, the surface energy varies from plane to plane. The structure of a small nucleus is not yet known, but if it is a polyhedron, the contribution of its edges and corners to the interfacial energy is significant. The term, ΔG_A, is also complex, because crystal growth involves both diffusion and a variety of surface processes, each of which has a characteristic activation energy.

A more empirical approach has been developed by Christiansen and Nielsen.[4] Their theory concerns itself with the nature of the induction period, which is the interval between the time of mixing two solutions to form a supersaturated solution and the time when precipitation is first observed. The following equation describes the relationship between the induction period and the concentration of the supersaturated solution of many slightly soluble salts:

$$k = C_0^p T,$$

where

C_0 = initial concentration of the supersaturated solution,
T = induction period,
k and p are constants.

Christiansen and Nielsen consider that the induction period represents the time required to build up clusters of size X_n, according to the mechanism previously outlined. They treat all reactions leading to X_n as steady-state processes; by assuming that X_n is different from smaller clusters in that it is more likely to gain another ion than to lose one, and that precipitation is observed when a constant fraction of the solute has deposited, they were able to derive the above equation, and to identify p as $n - 1$, where n is the total number of ions in the nucleus.

The above two theories are apparently in opposition, inasmuch as the classical theory predicts that, (*a*) the size of the nucleus varies with supersaturation, and (*b*) the rate of nucleation depends very drastically upon supersaturation, which signifies a large nucleus. The Christiansen–Nielsen theory predicts a constant nucleus size and a much less drastic dependence of nucleation rate on supersaturation, thus indicating a relatively small nucleus. Support of one or the other of these viewpoints by comparison of experimental results has not yet been possible, both because of theoretical and operational uncertainties, and because the theories have been derived to fit essentially different cases. The classical theory assumes that supersaturation is built up homogeneously and extremely slowly until a critical supersaturation is reached; that is, steady-state concentrations of clusters of various sizes are always present in the solution, and precipitation is observed when the supersaturation is increased enough to shift the concentrations so that there is an appreciable concentration of clusters X_n. The Christiansen–Nielsen theory assumes that the supersaturated solution initially contains no clusters of any size, and that some finite time interval is required to form the nuclei *via* a steady-state process, with precipitation again occuring when there is an appreciable concentration of clusters X_n. Thus, the two theories may not be actually contradictory. Progress toward harmonizing them has been made by Collins,[6] who introduces the induction period into the classical theory.

EXPERIMENTAL ASPECTS AND DISCUSSION

The greatest conflict between the two theories lies in the often contradictory experimental results which are obtained, depending on the approach used. When two solutions are mixed to form a supersaturated solution, an induction period is usually observed, and a small nucleus size is calculated.[4] If the supersaturation is built up slowly, a critical supersaturation below which precipitation will not occur is observed, and a large nucleus size is calculated.[14]

The results of induction period measurements for a number of slightly soluble salts have been summarized by Nielsen.[16] They indicate that nuclei of these salts are small; examples are $(Ag_2CrO_4)_2$, $(CaF_2)_3$, and $(AgCl)_3$. In Christiansen and Nielsen's work,[4] rapid-flow kinetic methods were used to study a wide range of induction periods, the time scales extending over an interval of from four to six powers of ten; straight line plots of the log of salt concentration vs. the log of the induction period were obtained. Other investigators (*cf.* reference 16), working in more limited concentration ranges, also obtained straight line plots.

Because it affords a means for slowly and homogeneously increasing the concentration of a salt from virtually zero to the critical value, the technique of precipitation from homogeneous solution has been used with success in studies of nucleation. LaMer and Dinegar[14] have used this method of precipitation, as well as direct mixing techniques, as outlined previously, in their studies of the precipitation of barium sulphate.

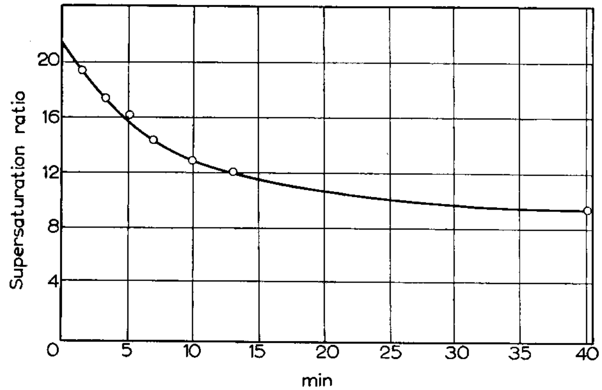

FIG. 1.—Time of appearance of crystalline phase ($BaSO_4$) as a function of supersaturation ratio, by direct mixture of solutions.[14]

In the latter experiments, these investigators rapidly mixed dilute solutions of varying concentrations of barium nitrate and sodium sulphate, and examined the resulting solutions for the time of appearance of barium sulphate crystals. The results are shown in Fig. 1. The supersaturation ratio, S, is again defined as

$$(K_{\text{I.P.}}/K_{\text{S.P.}})^{1/2}.$$

For supersaturation ratios above 12, the time of appearance of crystals was sharp and well defined. For ratios below 12, there was no sharp transition point. Their data, combined with those of Christiansen and Nielsen,[4] give a nucleus consisting of seven ions, either $[Ba_4(SO_4)_3]^{2+}$ or $[Ba_3(SO_4)_4]^{2-}$.

When barium was precipitated from homogeneous solution, by generating sulphate by the reaction,

$$S_2O_8^{2-} + 2S_2O_3^{2-} = 2SO_4^{2-} + S_4O_6^{2-},$$

precipitation became apparent at a constant supersaturation ratio. This "critical" supersaturation ratio, S_c, was found to be 21·5 ± 0·4 over the range of $(Ba^{2+}) = 5$ to $20 \times 10^{-4}M$. This compares favourably with the value of 21·2 obtained from Fig. 1 by extrapolation to zero time. LaMer and Dinegar modify the Kelvin equation as follows, for the nucleation of a salt from solution:

$$iRT/M \ln S_c = 2\sigma/\rho r,$$

where

i = van't Hoff factor,
M = molecular weight,
S_c = critical supersaturation,
σ = interfacial tension,
ρ = density,
r = radius of nucleus.

Using the values 21·5 for S_c, and 1500 dynes/cm for σ, they calculate that $r = 0{\cdot}01\mu$ for $BaSO_4$.

Although the values of the critical supersaturation ratio found by LaMer and Dinegar are remarkably constant, it appears that the nucleation which occurs is heterogeneous rather than homogeneous, *i.e.*, it involves foreign bodies. Collins and Leineweber[7] have repeated the experiments of LaMer and Dinegar and have found that the observed supersaturation ratio, although again remarkably constant for a given set of experiments, is nevertheless strongly dependent upon the purity of the reagents. Impurities present in the sodium thiosulphate obtained from commercial sources proved very effective in lowering the critical supersaturation ratio. Upon purification of the reagents by recrystallizations and successive filtrations, a maximum supersaturation ratio of about 32 was obtained; when no attempts were made to remove impurities, the value was 19. "Critical" supersaturations between these two values were also obtained, depending on the rigour of the purification. Collins and Leineweber conclude that the nucleation process in their experiments is probably heterogeneous but that further purification of the materials used would be required for a firm conclusion with regard to this point.

In precipitation by direct mixing, several investigators have observed effects which can be explained by assuming that heterogeneous nucleation is involved. Bogan and Moyer[3] find that the final size of particles of precipitated barium sulphate depends on the age of the barium chloride solution used in the precipitation. Aged solutions, or solutions filtered through a 2 to 5 micron Selas crucible, produced crystals seven to ten times as large as those from fresh, unfiltered barium chloride. They attribute this to fragments of the barium chloride lattice which remain undissolved and act as nuclei for the precipitation. Benedetti-Pichler[2] has observed a similar effect. He attributes nucleation to impurities in the barium chloride; these impurities, during ageing, are removed by adsorption on the walls of the storage vessel. Nielsen[17] has studied the relationship between the number of particles of barium sulphate precipitate and the rigour of cleaning of the reaction vessels. With ordinary methods of cleaning he obtains about 2000 particles/mm^3; when his vessels are cleaned by steaming, this decreases to about 100/mm^3, and in some cases to as low as 25/mm^3. Nielsen believes that the most reasonable explanation for these observations is that suitable nuclei exist in the system before the solutions are mixed, although this explanation makes the significance of the nucleus sizes obtained by his theory rather questionable. This effect of impurities on the critical supersaturation may explain some of the conflicting results obtained by various investigators. Cobbett and French[5] found that $BaSO_4$ would not precipitate below a $K_{\text{I.P.}}$ of $1{\cdot}59 \times 10^{-8}$; LaMer and Dinegar[14] measured an induction period of about 12 minutes for this concentration. For AgCl of $K_{\text{I.P.}}$ below $3{\cdot}14 \times 10^{-10}$, Davies and Jones[8] found that no precipitation took place even after 18 hours, while Kobayashi[12] obtained an induction period of about 25 minutes for this concentration. It is also interesting to note from the data of LaMer and Dinegar that the crystalline phase appears in 10 minutes (*cf.* Fig. 1) for an initial supersaturation ratio of 13 in a direct-mixing experiment, whereas calculation shows that 60 minutes (*cf.* run No. 9 of Table I of reference 14) are required to proceed from a supersaturation ratio of 13 to the value of about 21 required for nucleation in the case where sulphate is slowly generated by the chemical method.

Turnbull[19] has investigated the kinetics of precipitation of barium sulphate using direct-mixing experiments and finds that the rate of precipitation of the salt is dependent, for a given initial supersaturation ratio, upon the relative concentrations of the solutions being mixed and on the method of mixing. For example, when equal amounts of barium hydroxide of concentration $2m_0$ and sulphuric acid of concentration $2m_0$ are mixed to produce a solution of barium sulphate of initial concentration m_0, the fraction of barium sulphate precipitated in 20 minutes is about 0·48, whereas the fraction precipitated in the same time is about 0·05 when barium hydroxide of concentration $215m_0$ and sulphuric acid of concentration m_0 are rapidly mixed to produce barium sulphate of initial concentration m_0.

Turnbull's data are presented as curves showing the relation between X, the fraction of barium sulphate precipitated, and t, the time. By multiplying the time scale by a suitable factor f the composite curves are superimposable. The course of precipitation can thus be described by the general relation:

$$\mathrm{X} = F(f\,.\,t),$$

where f depends on the supersaturation ratio S, the method of mixing and the specific solutions used. Turnbull interprets this relation as indicating that the number of precipitation nuclei formed after homogenization of the solution is negligible in comparison with the number produced during the homogenization (mixing) process. The dependence of X on $(f\,.\,t)$ is then determined by the rate of growth of the n_i particles which were formed during homogenization. For the most reproducible method of mixing, Turnbull estimates that the number of nuclei formed is 560 times greater for S equal to 19·0 than for S equal to 12·2.

It is surprising, as Turnbull indicates, that a slower rate of precipitation is obtained with the method that might be expected to produce the higher local excess of supersaturation, namely, addition of a relatively concentrated barium solution. Turnbull also observed a similar effect when barium nitrate and potassium sulphate were used. However, in those cases where a concentrated sulphate solution was added to the barium solution, the rate of precipitation was much faster than in the opposite case. Turnbull states that "the effect may be associated with the use of a very small volume of a particular solution rather than with the mixing method". Dependence of the induction period and precipitation rate on the method of mixing has also been observed by Lucchesi[15] with $BaSO_4$ and with $SrSO_4$, and by Davies and Jones[8] with AgCl.

O'Rourke and Johnson[18] are in disagreement with Turnbull's view that the number of nuclei of barium sulphate formed after homogenization is small compared to that formed in the homogenization process itself. They base their argument that nuclei are formed *after* homogenization on their observation that the number of particles of barium sulphate formed is nearly independent of concentration when equal volumes of reagents of equimolar solutions of barium and sulphate were mixed. The concentrations of the solutions mixed ranged from 2·5 to $25 \times 10^{-4}M$; after rapid mixing and allowing the solution to stand until precipitation was complete, the particles of barium sulphate were counted. The number of particles per litre amounted to about $1{\cdot}2 \times 10^9$ (*cf.* the value of 10^8 obtained by Nielsen[17]) over the range of concentrations studied. In view of Nielsen's observation of the effect of cleaning of reaction vessels on the number of particles, it is possible that the constant number of particles formed was due to a fixed concentration of foreign nuclei, *i.e.*, heterogeneous nucleation could occur on each foreign nucleus, thus resulting in a constant number of particles.

Although it would appear that precipitation from homogeneous solution should avoid the effect of mixing fluctuations and some of the attendant uncertainities, O'Rourke and Johnson believe that other complications might arise because of the steadily increasing flow of nuclei brought into the crystal growth reaction stage. However, once the formation of crystals is effected, the solution concentration rapidly decreases to a value below the auto-nucleation point. In addition, the rate of formation of a reactant in precipitation from homogeneous solution is usually quite small, so that at any one time there will not be any great excess of the reactant, particularly in the presence of crystals. It thus does not seem reasonable to expect that new nuclei will be formed during precipitation from homogeneous solution in the presence of solid phase unless the critical supersaturation ratio is very small or the influx of precipitant is extremely high. Examination of crystals formed by the process of precipitation from homogeneous solution does not reveal the presence of small crystals; in fact, the crystals are usually quite large and fairly uniform in size.

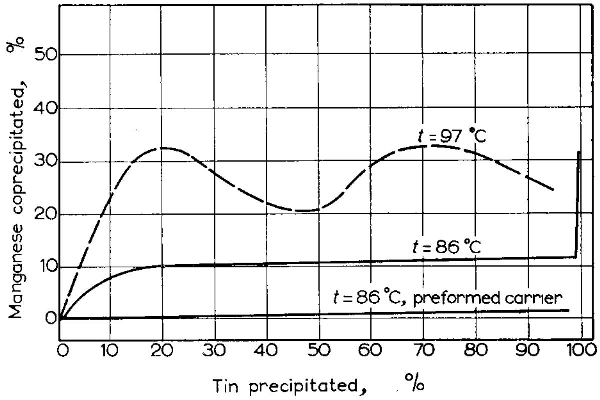

FIG. 2.—Co-precipitation of manganese with basic stannic sulphate precipitated from homogeneous solution.

Davies and Jones[8] have studied the precipitation of silver chloride to determine its critical supersaturation.

These investigators mixed dilute solutions of silver nitrate and potassium chloride and determined the change of conductance with time. By extrapolating a plot of the average rate of fall in conductivity for very slow precipitations over the first hour or two after mixing against ionic concentration product, Davies and Jones found the critical ionic concentration product at which nucleation occurred to be $3{\cdot}14 \times 10^{-10}$. These authors give the ion activity product constant, $K_{\text{S.P.}}$, as $1{\cdot}81 \times 10^{-10}$; the supersaturation ratio is thus of the order of 1·3. In these experiments the initial ionic ratio of [Ag^+] to [Cl^-] was one. When the ratio was varied, from 0·25 to 4, it was found that a critical supersaturation limit existed for each case, but that the supersaturation product depended on the ionic ratio.

Davies and Jones obtained the same values for the critical supersaturations in a different way, by carrying out moderately slow precipitation runs and by plotting the rate of precipitation against the amount of AgCl precipitated. They found that precipitation accelerated to a maximum, and that shortly thereafter the rate curve changed at a fairly well-defined point to a nearly linear rate of decrease. The turning-point at which the change takes place was interpreted as the stage at which fresh nuclei ceased to be formed. The concentration products at the turning-point correlated well with the critical concentration products obtained by the previous method. It would be of considerable interest to determine if the variable concentration product obtained with different [Ag] to [Cl] ratios would be constant if the technique of precipitation from homogeneous solution were applied in a manner similar to that by LaMer and Dinegar in the case of barium sulphate.

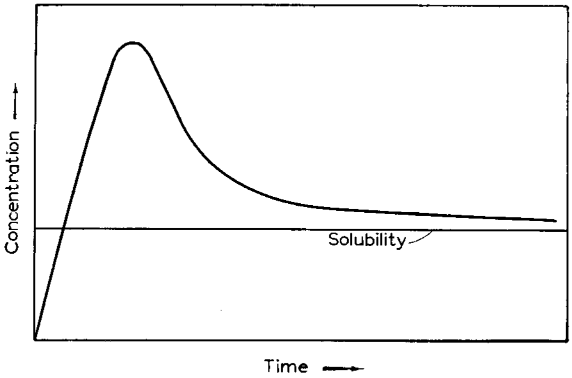

FIG. 3.—Schematic representation of concentration of elemental sulphur formed during precipitation from homogeneous solution.

The investigation of Gordon, Teicher and Burtt[10] showed the effect of the nucleation process on co-precipitation. The results are shown in Fig. 2. When basic stannic sulphate was precipitated in the presence of manganese[11] by hydrolysing urea at 97°, the extent of co-precipitation of the manganese as a function of the fraction of tin precipitated followed a somewhat erratic pattern. When the rate of precipitation of basic stannic sulphate was made smaller, by hydrolysing urea at 86°, it was found that co-precipitation of manganese occurred in the early stages of the precipitation process where less than 25% of the tin present was precipitated and that from that point on there was virtually no co-precipitation of manganese until the fraction of tin precipitated reached the value of about 99%, at which value the removal of manganese began to be appreciable. As can be seen from Fig. 2, the co-precipitation curve (eliminating the portion due to the initial rise) is characteristic of a system of small distribution coefficient.[11] As is also shown in Fig. 2, the presence of pre-formed basic stannic sulphate eliminated the initial co-precipitation. Basic stannic sulphate was allowed to nucleate and precipitate to the extent of about 25% of the total present but without manganese initially present in the reaction mixture. Manganese was then added and the reaction allowed to proceed in order to precipitate different fractions of the tin present. As can be seen from the figure, the co-precipitation curve is identical, although displaced downward, to that obtained when manganese was initially present.

LaMer and Dinegar[13] have proposed a model for precipitation from homogeneous solution which explains these observations. Fig. 3 is essentially their plot of concentration vs. time for the precipitation of sulphur. The concentration increases with time until the critical supersaturation ratio is reached, whereupon nucleation occurs. The initial rate of precipitation is quite rapid because of the high supersaturation. Not until the supersaturation has decreased appreciably does the slow process characteristic of precipitation from homogeneous solution take place. Extending this scheme to the observations of Gordon, Teicher and Burtt, the anomalous early co-precipitation can be attributed to the high supersaturation required for nucleation, and the resultant initial non-homogeneous precipitation. In the experiments with pre-formed carrier, manganese was not added until the initial supersaturation of the system was relieved and precipitation was occurring at a controlled rate.

CONCLUSION

The relationships between nucleation and the properties of a precipitate will undoubtedly be more fully developed as the nucleation process is further elucidated. The classic investigation of von Weimarn[22] was instrumental in establishing some of the basic rules used by analytical chemists in precipitation, such as using dilute solutions of reagents, adding the precipitant slowly and using vigorous stirring. These precipitation rules were suggested primarily as a guide to produce more nearly perfect growth of the crystals of precipitate by controlling supersaturation. Nucleation studies carried out thus far indicate that these precipitation rules will need revision in some cases to allow for the effect of nucleation. Turnbull[19] finds that barium sulphate precipitates more slowly and presumably more perfectly, when a highly concentrated reagent is added rapidly to a dilute one as opposed to the mixing of two dilute solutions. Nielsen[17] finds that stirring during the early stages of precipitation fractures the small crystallites to form more nuclei, and thus leads to a greatly diminished final particle size. Such facts as these indicate the need for extending the precipitation rules to include nucleation phenomena. During the nucleation period the number of particles and the final size are fixed. Nucleation determines the surface area on which precipitation can take place, and consequently establishes the tempo of the precipitation. Further study of the nucleation process will be of great aid in understanding, and thus increasing the sensitivity and delicacy of separation by precipitation.

Zusammenfassung—Die Fällung beinhaltet zwei Prozesse: Kristallkeimbildung und anschliessendes Kristallwachstum. Der Vorgang der Kristallkeimbildung ist von ausserordentlicher Wichtigkeit für die Zahl und Grösse der am Ende vorhandenen Kristallpartikeln. Die Bedeutung von experimentellen Studien über Kristallkeimbildung wird erörtert und auf die Notwendigkeit weiterer Untersuchungen hingewiesen.

Résumé—La précipitation comporte deux processus: la formation des germes et la croissance subséquente des cristaux. La formation des germes a une très grande importance pour la détermination du nombre et de la taille des particules cristallines obtenues finalement. On discute l'importance des études expérimentales sur la nucléation et montre la nécessité de faire de plus amples recherches à ce sujet.

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DETERMINATION OF HYDRAZINE AND HYDRAZINE DERIVATIVES USING BROMINE MONOCHLORIDE AS STANDARD SOLUTION

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Summary—A method was evolved for the determination of hydrazine and hydrazine derivatives (such as phenylhydrazine, semicarbazide, *iso*-nicotinic hydrazide) with the use of standard bromine monochloride solution. The titration values are not affected by the degree of acidification or by the nature of the acid used.

On the basis of the experimental results the principle of the Kurtenacker method of hydrazine determination is interpreted.

SCHLÖTTER was the first to evolve a bromometric method for the determination of hydrazine. His method, however, yielded only approximate values, due to interfering side reactions. The use of copper and iron salts or molybdate as catalysts capable of eliminating these side reactions was suggested by Hodgkinson.[2] Conditions of oxidizing hydrazine by potassium bromate were studied by Browne and Shetterly[3] who found that in a sulphuric acid medium hydrazine is oxidized to hydrazoic acid and ammonia.

The first precise bromometric method, which is still in use, for the determination of hydrazine was evolved by Kurtenacker and Wagner,[4] who determined hydrazine in strong hydrochloric acid, in the presence of indigo carmine as indicator, by direct titration with a standard bromate solution. The Kurtenacker method has been subjected to a thorough critical examination by Kolthoff[5] who found that the accuracy of the method depends to a great extent on the concentration of hydrochloric acid. When the solution initially contains hydrochloric acid in concentrations below 20%, the results will be lower than the actual values. The precision of the method is reduced because the indigo carmine indicator consumes bromate. Methyl red, proposed by Kolthoff, behaves similarly.

The use of *p*-ethoxychrysoïdine as an indicator in bromometry was suggested by Schulek and his co-workers[6]. Wojahn[7] actually applied this indicator to the bromometric determination of *iso*nicotinic hydrazide.

Conditions for the bromometric determination of hydrazine and its derivatives in the presence of *p*-ethoxychrysoïdine as indicator were examined by Laszlovszky.[8] It appeared that with low concentrations of hydrochloric acid the method yielded low values. When high concentrations of hydrochloric acid were applied, the results were affected by consumption of bromate by the indicator.

As this short literature survey discloses, the bromometric determination of hydrazine and hydrazine derivatives yields reliable results only under strictly controlled experimental conditions.

In the course of our earlier experiments,[9] we succeeded in preparing a 0·1N standard solution of bromine monochloride the titre of which showed changes of not more than 3–5% after storage for 2–3 months under appropriate conditions. An attempt was made to determine hydrazine and hydrazine derivatives by a standard solution of bromine monochloride. The preparation and properties of the standard solution have been discussed elsewhere in detail[9]. The solution was stored in a Winkler burette with a stock flask.

The titre of the standard solution was determined by iodometry. The titre of the reagent was established daily. *p*-Ethoxychrysoidine was applied as indicator. The effect of the nature and concentration of acid on the titration results were examined.

EXPERIMENTAL

Determination of hydrazonium sulphate

It was previously established that hydrazine is quantitatively oxidized to elementary nitrogen by bromine monochloride, as shown by the equation:

$$N_2H_4 + 2BrCl \rightarrow N_2 + 2HBr + 2HCl$$

In this reaction the equivalent weight of hydrazine is equal to 1/4 of its molecular weight (32·53).

Experiments were carried out to establish how changes in the nature and concentrations of acids affect the results of measurements. A 0·2% ethanolic solution of *p*-ethoxychrysoïdine was applied as indicator.

It can be seen from Table I that the degree of acidification and the nature of acid applied do not affect the reaction. Moreover, an aqueous solution of hydrazine sulphate can be titrated directly with bromine monochloride solution, without any acidification.

No deviations were observed between the results of titrations conducted in the presence of sulphuric and hydrochloric acid. The only difference was that in the case of quick titration, the indicator was consumed more rapidly in a sulphuric acid medium than in a hydrochloric acid solution. One extra drop of indicator was required in such cases, the addition of which did not affect the titration results. (This phenomenon is attributed to the fact that the higher chloride content of the hydrochloric acid solution suppresses the dissociation of the bromine monochloride complex, thus reducing the redox potential.[9])

It appears from Table I that hydrazine sulphate can be determined with an appreciable precision by means of standard bromine monochloride. The maximum titration error ranges were 0·2%.

It is known[10] that hydrazine sulphate is a non-hygroscopic substance of stoichiometric composition which can readily be purified by recrystallisation and dried at 150°. This is why it is frequently used in acidimetry as a primary standard.

On this basis, hydrazine sulphate is suggested as a primary standard for bromine monochloride solution.

Determination of phenylhydrazine hydrochloride

The reaction which takes place during the titration of phenylhydrazine with bromine monochloride

$$C_6H_5NH{\cdot}NH_2 + 2BrCl + H_2O = N_2 + C_6H_5OH + 2HBr + 2HCl,$$

has been subjected to investigation. The equivalent weight of phenylhydrazine in this reaction is equal to 1/4 of its molecular weight (36·14).

It was found that, as for hydrazine, the degree of acidification and the nature of the acid applied did not affect the determination (Table II).

It is of interest to note that solutions containing *p*-ethoxychrysoïdine as indicator, when allowed to stand for a while after titration, turn red in 15–20 minutes, because of the reducing action of the phenol formed in the oxidation of phenylhydrazine.

TABLE I.—RESULTS OF HYDRAZINE DETERMINATIONS

No.	Hydrazine sulphate, weighed, *mg*	0·1*N* BrCl, consumed, *ml*	Hydrazine sulphate, found, *mg*	Deviation		Acidification	
				mg	%	20% HCl, *ml*	2*N* H_2SO_4, *ml*
1	18·26	5·61	18·25	−0·01	−0·05	2	—
		5·61	18·25	−0·01	−0·05	2	—
		5·63	18·32	+0·06	+0·3	5	—
		5·61	18·25	−0·01	−0·05	5	—
		5·61	18·25	−0·01	−0·05	10	—
		5·61	18·25	−0·01	−0·05	10	—
2	15·15	4·65	15·13	−0·02	−0·13	—	—
		4·65					
		4·65	15·13	−0·02	−0·13	5	—
		4·65					
		4·65	15·13	−0·02	−0·13	—	10
		4·65					
3	30·05	9·25	30·09	+0·04	+0·13	—	—
		9·25					
		9·25	30·09	+0·04	+0·13	5	—
		9·23	30·03	−0·02	−0·06	5	—
		9·25	30·09	+0·04	+0·13	—	10
		9·25				—	10
		9·25	30·09	+0·04	+0·13	—	20
		9·25				—	20
4	36·21	11·13	36·21	0·00	0·00	2	—
		11·13					
		11·12	36·18	−0·03	−0·08	5	—
		11·13	36·21	0·00	0·00	5	—
		11·13	36·21	0·00	0·00	10	—
		11·13					

Determination of semicarbazide hydrochloride

The oxidation of semicarbazide, in direct titration with bromine monochloride, takes place according to the scheme

$$NH_2NH{\cdot}CO{\cdot}NH_2{\cdot}HCl + 2BrCl + H_2O \rightarrow N_2 + NH_4Cl + CO_2 + 2HBr + 2HCl.$$

The equivalent weight is equal to 1/4 of the molecular weight (27·88).

As before, the oxidation of semicarbazide by bromine monochloride is not affected, either, by the degree of acidification or the nature of acid (Table III).

It must be noted that in the case of semicarbazide the colour change of the indicator is not as

TABLE II.—RESULTS OF DETERMINATIONS OF PHENYLHYDRAZINE

No.	Phenylhydrazine hydrochloride weighed, *mg*	$0{\cdot}1N$ BrCl consumed, *ml*	Phenylhydrazine hydrochloride, found, *mg*	Deviation		Acidification	
				mg	%	20% HCl, *ml*	$2N$ H_2SO_4 *ml*
1	12·15	3·37	12·18	+0·03	+0·2	2	—
		3·37					
		3·37	12·18	+0·03	+0·2	5	—
		3·37					
		3·37	12·18	+0·03	+0·2	10	—
		3·37					
2	15·55	4·30	15·54	−0·01	−0·06	—	—
		4·30					
		4·30	15·54	−0·01	−0·06	5	—
		4·31	15·58	+0·03	+0·2	5	—
		4·29	15·50	−0·05	−0·3	—	10
		4·30	15·54	−0·01	−0·06	—	10
		4·30	15·54	−0·01	−0·06	—	20
		4·30					
3	24·10	6·69	24·18	+0·08	+0·3	2	—
		6·67	24·10	0·00	0	2	—
		6·67	24·10	0·00	0	5	—
		6·67					
		6·67	24·10	0·00	0	10	—
		6·69	24·18	+0·08	+0·3	10	—
		6·67	24·10	0·00	0	—	20
		6·67					
4	30·83	8·50	30·72	−0·11	−0·4	5	—
		8·50					
		8·50	30·72	−0·11	−0·4	—	10
		8·49	30·68	−0·15	−0·5	—	10
		8·50	30·22	−0·11	−0·4	—	20
		8·50					

readily observed as with other hydrazine derivatives. The colour of the indicator entirely disappears 0·5 to 1·0 drop before the end point, and it turns yellow only when a further half or whole drop is added, whereas with other hydrazine derivatives the colour change of the indicator takes place instantly, on adding a fraction of a drop. However, the application of an indicator correction is not considered necessary.

TABLE III.—RESULTS OF DETERMINATIONS OF SEMICARBAZIDE

No.	Semicarbazide hydrochloride, weighed, *mg*	0·1*N* BrCl consumed, *ml*	Semicarbazide hydrochloride, found, *mg*	Deviation		Acidification	
				mg	%	20% HCl *ml*	$2N\ H_2SO_4$ *ml*
1	16·59	5·97 5·97	16·65	+0·06	+0·36	2	—
		5·96	16·62	+0·03	+0·2	5	—
		5·97	16·65	+0·06	+0·36	5	—
		5·96 5·96	16·62	+0·03	+0·2	10	—
		5·96 5·96	16·62	+0·03	+0·2	—	10
		5·97	16·65	+0·03	+0·2	—	20
		5·96	16·62	+0·06	+0·36	—	20
		5·96 5·96	16·62	+0·03	+0·2	—	—
2	32·90	11·77 11·77	32·82	−0·08	−0·24	5	—
		11·76	32·79	−0·11	−0·3	—	10
		11·77	32·82	−0·08	−0·24	—	10
		11·76	32·79	−0·11	−0·3	—	20
		11·77	32·82	−0·08	−0·24	—	20

Determination of iso*nicotinic hydrazide*

*iso*Nicotinic hydrazide, can also be titrated with a 0·1*N* solution of bromine monochloride. The reaction proceeds according to the equation:

$$C_5H_4NCO{\cdot}NH{\cdot}NH_2 + 2BrCl + H_2O \rightarrow N_2 + C_5H_4NCOOH + 2HBr + 2HCl.$$

The equivalent weight is equal to 1/4 of the molecular weight (34·28).

The results are not affected by the nature of the mineral acid or by its concentration (Table IV). In contrast to the previous compounds, *iso*nicotinic hydrazide does not undergo acid hydrolysis on dissolving, therefore it cannot be measured without acidification (too low values). When, however, it is converted into its hydrochloride or sulphate, it is suitable for titration with bromine monochloride solution without further acidification.

TABLE IV.—RESULTS OF DETERMINATIONS OF *iso*NICOTINIC HYDRAZIDE

No.	*iso*Nicotinic hydrazide, weighed, *mg*	0·1*N* BrCl, consumed, *ml*	*iso*Nicotinic hydrazide, found, *mg*	Deviation		Acidification	
				mg	%	20% HCl, *ml*	2*N* H_2SO_4, *ml*
1	18·01	5·24	17·96	−0·05	−0·3	2	—
		5·26	18·03	+0·02	+0·1	2	—
		5·24	17·96	−0·05	−0·3	5	—
		5·24					
		5·26	18·03	+0·02	+0·1	10	—
		5·27	18·06	+0·05	+0·3	10	—
		5·24	17·96	−0·05	−0·3	—	20
		5·26	18·03	+0·02	+0·1	—	20
2	15·22	4·37	14·98	−0·24	−1·6	—	—
		4·37					
		4·46	15·29	+0·07	+0·5	—	10
		4·46					
		4·43	15·19	−0·03	−0·2	—	20
		4·46	15·29	+0·07	+0·5	—	20
		4·46	15·29	+0·07	+0·5	5	—
		4·43	15·19	−0·03	−0·2	5	—
3	30·17	8·66	29·69	−0·48	−1·6	—	—
		8·66					
		8·78	30·10	−0·07	−0·2	5	—
		8·77	30·06	−0·11	−0·4	5	—
		8·85	30·34	+0·17	+0·6	—	20
		8·82	30·23	+0·06	+0·2	—	20
		8·82	30·23	+0·06	+0·2	—	10
		8·82					
4	35·71	10·38	35·58	−0·13	−0·4	5	—
		10·38					
		10·38	35·58	−0·13	−0·4	10	—
		10·32	35·38	−0·33	−0·9	10	—

Procedure for hydrazine and hydrazine derivatives

On the basis of the experiments described the following method is proposed for the determination of hydrazine and hydrazine derivatives.

About 0·30 g substance is weighed accurately, transferred quantitatively into a 100-ml measuring flask and made up to volume with distilled water. 5–10-ml portions of this stock solution are diluted with distilled water to 30–50 ml, and 2–10 ml of 20% hydrochloric acid or 10–20 ml of $2N$ sulphuric acid and 1 drop of *p*-ethoxychrysoïdine indicator are added. The resulting solution is titrated with $0{\cdot}1N$ bromine monochloride solution.

1 ml of $0{\cdot}1N$ bromine monochloride is equivalent to 2·253 mg of hydrazine sulphate, 3·614 mg of phenylhydrazine hydrochloride, 2·788 mg of semicarbazide hydrochloride or 3·428 mg of *iso*nicotinic hydrazide.

DISCUSSION

As a result of these experiments the principle of the bromometric determination of hydrazine by the Kurtenacker method[4] can be interpreted.

In sulphuric acid, hydrazine is known to react with bromate to form hydrazoic acid and ammonia,[3] whereas in strong hydrochloric acid a nearly instantaneous reaction between bromate and hydrochloric acid takes place, with formation of bromine monochloride. In the Kurtenacker method[4] for hydrazine, bromine monochloride developed in this way during titration oxidizes hydrazine to elementary nitrogen, and thus controls the oxidation.

The rate of the reaction between bromate and hydrochloric acid diminishes with decreasing concentration of hydrochloric acid. Thus, bromate can react directly with hydrazine, and this side reaction is responsible for deviations in results. In titration with a solution of bromine monochloride, therefore, acidification with hydrochloric acid is not necessary.

Zusammenfassung—Es wird eine Methode für die Bestimmung von Hydrazin und seinen Derivaten (z.B. Phenylhydrazin, Semicarbazid, *iso*-Nikotinsäurehydrazid) mit einer Brom-chlorid-Masslösung entwickelt.

Die Titrations-Werte werden von Art und Menge der Säure nicht beeinflusst.

Auf Grund der exprimentellen Resultate konnte das Prinzip der Kurtenacker-Methode für die Bestimmung von Hydrazin erklärt werden.

Resume—On a élaboré une méthode pour le dosage de l'hydrazine et des dérivés de l'hydrazine (tels que la phénylhydrazine, le semicarbazide, l'hydrazine *iso*nicotique) au moyen d'une solution titrée de chlorure de brome. Les valeurs du titrage ne sont affectées ni par le degré d'acidité ni par la nature de l'acide utilisé.

Par suite des résultats expérimentaux on a interprété la principe de la méthode de Kurtenacker pour le dosage de l'hydrazine.

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GRAVIMETRIC DETERMINATION OF OSMIUM WITH 1:2:3-BENZOTRIAZOLE

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Summary—A method for the direct gravimetric determination of osmium with 1:2:3-benzotriazole in acetic acid-sodium acetate buffer is presented. The method is accurate and reproducible, and the conditions used in the determination are not critical. The precipitate is a stoichiometric compound which is stable from room temperature up to 200°. It appears that 1:2:3-benzotriazole is probably the first organic reagent to be used successfully in the direct gravimetric determination of osmium.

THE gravimetric determination of osmium[1,3] has been a subject of study in recent years. Thionalide was reported[1] as the first organic reagent to be used successfully for the indirect gravimetric determination of osmium. In these studies, strychnine sulphate, and certain substituted thioureas and thiazoles were recommended for the gravimetric or colorimetric determination of osmium. Though osmium is easily separated from the other platinum metals as its volatile tetroxide by distillation, its quantitative titrimetric and gravimetric determinations[1,3,4] are tedious and/or time consuming. However, in the aforementioned gravimetric procedure for osmium with thionalide, Wagner, Hall, and Markle[5] have given a detailed account of the gravimetric determination of osmium with thionalide which would seem to require approximately 15 hours for a single determination.

Since there is great need for a rapid and direct method for the gravimetric standardization of osmium in solution, the present investigation is concerned with a determination of osmium with 1:2:3-benzotriazole which is direct and involves a stoichiometric compound, whose pH of precipitation in acetic acid-sodium acetate buffer and drying temperature are not critical, and which requires less than 2 hours for a complete determination.

EXPERIMENTAL

Reagents and solutions

A 2.0153-g sample of osmium tetroxide, obtained from A. D. Mackay, Inc., was dissolved in 500 ml of 0.2*M* sodium hydroxide and diluted to 1 litre with distilled water using the procedure of Ayres and Wells.[2] This solution was standardized by the method of Klobbie.[4] All other materials used were reagent-grade chemicals. All precipitates were filtered using medium-porosity, sintered-glass crucibles.

Apparatus

A Beckman Model H2 Glass electrode pH meter was employed to take pH readings. Osmium tetroxide was distilled from solution using a modification of the distillation apparatus described by Westland and Beamish.[6]

Properties of osmium–1:2:3-benzotriazole precipitate

The interaction of osmium with 1:2:3-benzotriazole in acid media[7] gives a beige precipitate when precipitated from solution and after drying. Temperatures up to 200° were safe for drying as indicated graphically by thermogravimetric data presented by Wilson and Baye.[8] Constant weight was obtained for the precipitates after they had been dried at 110° for 30 minutes. The precipitates are readily coagulated in acetic acid-sodium acetate buffer. The effect of pH on precipitation of osmium by the recommended procedure given below is shown in Table I in which varying amounts of acetic acid were added. The pH of the solution containing the red coloured complex before addition of any acetic acid was 7.7. On the addition of acetic acid, the precipitate which began first to form at a pH of 4.2 was not coagulated.

Table I.—Effect of pH on precipitation of 15.08 milligrams of osmium

pH	Wt. of ppt. *mg*	Os found *mg*
7.7	—	—
4.2	—	—
4.0	47.6	15.13
4.0	47.4	15.06
4.0	47.5	15.10
3.5	47.5	15.10
3.5	47.4	15.06
3.5	47.5	15.10
3.0	47.5	15.10
3.0	47.5	15.10
3.0	47.5	15.10
2.7	47.5	15.10
2.7	47.5	15.10
2.7	47.6	15.13
2.5	47.6	15.13
2.5	47.5	15.10
2.5	47.5	15.10
2.3	47.5	15.10
2.3	47.4	15.06
2.3	47.4	15.06

Recommended procedure

Ten millilitres of the standard osmium solution which contained 1.51 mg of Os per ml were added to a flask containing 1 ml of ethanol. To this solution were added 25 ml of 2% aqueous 1:2:3-benzotriazole to form the red complex. After heating the solution containing the red complex on a steam bath for 15 minutes, the pH is adjusted roughly to 3 using acetic acid. The resulting precipitate and solution are digested for 15 minutes to coagulate the precipitate. Then the precipitate is filtered on a weighed, medium-porosity, sintered-glass crucible and washed several times with hot distilled water. The precipitate is dried at 110° for 1 hour to constant weight. The theoretical factor for osmium corresponding to the formula $Os(OH)_3(C_6H_4NHN_2)_3$ is 0·3178, the value used to calculate the osmium content of the precipitate. Experimental data shown in Table II were in good agreement with the theoretical factor 0.3178.

Data obtained from several determinations of osmium, after distilling this element as its tetroxide from nitric acid solution, are shown in Table III. The osmium tetroxide was distilled over into 0.1*M* sodium hydroxide using a distillation apparatus similar to the one described by Westland and Beamish.[6]

DISCUSSION

A gravimetric method for the direct determination of osmium is presented, which involves the precipitation of osmium as $Os(OH)_3(C_6H_4NHN_2)_3$. This method is applicable to the determination of osmium after having distilled this element as its

TABLE II.—GRAVIMETRIC DETERMINATION OF OSMIUM

Os taken *mg*	Wt. of ppt. *mg*	Os found *mg*	Difference *mg*
1.51	4.7	1.49	−0.02
1.51	4.8	1.53	+0.01
1.51	4.7	1.49	−0.02
3.02	9.5	3.02	0.00
3.02	9.6	3.05	+0.03
3.02	9.6	3.05	+0.03
4.52	14.2	4.51	−0.01
4.52	14.3	4.54	+0.02
4.52	14.1	4.48	−0.04
7.54	23.5	7.47	−0.07
7.54	23.7	7.53	−0.01
7.54	23.6	7.50	−0.04
12.06	38.1	12.11	+0.05
12.06	38.0	12.08	+0.02
12.06	37.9	12.04	−0.02
15.08	47.5	15.10	+0.02
15.08	47.4	15.06	−0.02
15.08	47.5	15.10	+0.02
22.62	71.1	22.60	−0.02
22.62	71.2	22.63	+0.01
22.62	71.1	22.60	−0.02

TABLE III.—GRAVIMETRIC DETERMINATION OF OSMIUM AFTER THREE DIFFERENT DISTILLATION SEPARATIONS

Osmium, *mg*	
Taken	Found
15.08	15.10
15.08	15.10
15.08	15.06

tetroxide from solution. The method is believed to offer certain advantages over the recently-published thionalide procedure. The osmium–1:2:3-benzotriazole procedure, as compared to the thionalide procedure, is direct, saves time, and the determination requires only simple equipment.

Acknowledgment—The authors wish to express their sincere thanks for a National Science Foundation grant which supported this study.

Zusammenfassung—Eine Methode zur direkten gravimetrischen Bestimmung von Osmium mittels 1:2:3-Benzotriazole in Essigsäure-Natriumacetat-Puffer wird angegeben. Die Methode ist genau, gut reproduzierbar und die Arbeitsbedingungen sind einfach. Der Niederschlag ist eine stöchiometrische Verbindung, die von Zimmertemperatur an bis auf 200° stabil ist. Es scheint, dass

1:2:3-Benzotriazol das erste organische Reagens ist, das in der direkten gravimetrischen Bestimmung von Osmium erfolgreich verwendet worden ist.

Résumé—Les auteurs présentent une méthode de dosage par gravimétrie directe de l'osmium par le 1:2:3-benzotriazol en tampon acide acétique-acétate de sodium. Cette méthode est précise et reproductible, et les conditions de dosage ne sont pas critiques. Le précipité est un composé stoechiométrique qui est stable de la température ordinaire jusqu'à 200°. Il est probable que le 1:2:3-benzotriazol est le premier réactif organique à être utilisé avec succès dans le dosage de l'osmium par gravimétrie directe.

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CERIMETRIC DETERMINATION OF URANIUM^{IV}

USE OF TRIPHENYLMETHANE DYES AS INTERNAL INDICATORS

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Summary—The use of the triphenylmethane dyes (erioglaucine, eriogreen, and xylene cynol FF) as internal indicators in the cerimetric titration of uranium^{IV} has been investigated. The titration is possible in the cold with sufficient rapidity and accuracy, the indicator colour change appearing sharply at the equivalence point. The indicator reactions are rapid and reversible within a wide range of acidity, from 0·5N to 8·0N, unlike other indicators, *e.g.* diphenylbenzidine, N-phenylanthranilic acid or ferroïn, which require specified conditions for their proper functioning. These indicators can also beused for titration of uranium^{IV} with ceric ammonium nitrate in perchloric acid medium (but not in nitric acid medium).

FURMAN and Schoonover[1] were the first to employ ceric sulphate for the titrimetric determination of a mixture of uranium^{III} and uranium^{IV}. The titration was carried out potentiometrically in an inert atmosphere at 80°. They found that the first break in the potential corresponds to the stoichiometric oxidation of uranium^{III} to uranium^{IV}, and the second break to the complete oxidation of uranium^{IV} to uranium^{VI}. According to Luyckx,[2] the end-point corresponding to the oxidation of uranium^{III} is accurate only when the titration is carried out at 80°. Heal[3] stated that the potential-break occurs too late at room temperature, probably because of the slow oxidation of the hydrogen layer by the titrant. Belcher, Gibbons and West[4] have used uranium^{IV} chloride as a titrimetric (reductimetric) reagent for the determination of permangante, dichromate, vanadate, iron^{III} and cerium^{IV}. They observed that in the potentiometric titration of dichromate, cerate, permanganate and vanadate solutions with uranium^{IV} it is necessary to work at elevated temperatures. They obtained satisfactory and consistent results when the titrations were carried out at 60°. In spite of the statements of earlier workers, we believe that the need for the use of a high temperature for the potentiometric titration of uranium^{IV} by ceric sulphate is not because of the sluggishness of the reaction between uranium^{IV} and cerium^{IV}, but because of the difficulty in the ready establishments of steady potentials. It is of interest to note in this connection that Belcher, Gibbons and West observed that although permanganate was decolorized in the cold by uranium^{IV}, no change in the oxidation potential of the system occurred. It may also be noted that even the reaction between uranium^{IV} and iron^{III} is reported to be rapid at room temperature, although the potentiometric titration of iron^{III} by uranium^{IV} requires a higher temperature. Rodden[5] has recorded the observations of Korach, Nessle, Sinclair and Casto on this reaction and writes as follows:—"The rate of oxidation of uranium^{IV} by iron^{III} in 5% sulphuric acid has been studied by means of the absorption maximum of uranium^{IV} at 650 mμ. Since it was found that the rate of oxidation is faster than the time of addition and the absorption measurements (approximately 1 min), it appears that titrations at room temperature would be feasible if some method could be found to speed the rate of establishment of potential equilibrium at the electrode."

Ferroïn was first used by Willard and Young[6] as an internal indicator for the cerimetric titration of uranium^{IV}. They found that it was necessary to raise the temperature to 50° to obtain a sharp end-point. Birnbaum and Edmonds[7] investigated the use of this indicator further and found that it does not function properly at 50°, because of its dissociation at the higher temperature. The pink colour fades perceptibly long before the end-point is reached, They found that in titrations where the approximate titre is not known, the ceric sulphate has to be added slowly, and the colour fades entirely, so that it is necessary to add more indicator near the end of the titration. Moreover, it becomes necessary to protect the solution from aerial oxidation. Birnbaum and Edmonds[7] are of the opinion that the titration at room temperature is unsatisfactory, apparently because of the slowness of the reaction between the ceric ion and quadrivalent uranium. These authors observed that in the presence of phosphoric acid the titration at room temperature gives a sharp end-point. In contrast to the earlier workers, Sill and Peterson[8] recently stated that the reaction between cerium^{IV} salt and uranium^{IV} is very rapid at room temperature. They found that "Sulphatoceric acid can be added to a dilute sulphuric acid solution of uranium^{IV} at the full speed of delivery of the burette without producing the yellow colour of excess of cerium^{IV}." Sill and Peterson adduced evidence in favour of the view that the beneficial action of phosphoric acid observed by Birnbaum and Edmonds is more concerned with the catalysis of the slow reaction between uranium^{IV} and the oxidized indicator than with the rection between uranium^{IV} and cerium^{IV}. Recently Pandurango Rao, Murty and Gopala Rao[9] have confirmed the findings of Sill and Peterson.

Vogel[10] states that the titration of uranium^{IV} with ceric sulphate can be carried out at 50°, using N-phenylanthranilic acid as indicator.

Pandurango Rao, Murty and Gopala Rao[9] have recently stated that the need for a higher temperature is not because of the slow speed of the reaction between uranium^{IV} and cerium^{IV} at room temperature but because of the unsatisfactory functioning of the indicators. They have developed suitable conditions for the titration of uranium^{IV} by ceric sulphate at the room temperature, with diphenylbenzidine or N-phenylanthranilic acid as indicators using suitable catalysts. We have now investigated the use of triphenylmethane dyes as internal indicators in this tiration. The dyes tested are erioglaucine A, eriogreen B and xylene cyanol FF. We have found that the reaction between the indicator and ceric sulphate is quite rapid even in very dilute solutions. For instance, the addition of a drop of $0{\cdot}01N$ ceric sulphate solution to 50 ml of $1{\cdot}0N$ sulphuric acid solution, containing 0·5 ml of a 0·1% solution of the dye, changes the colour immediately from yellow to orange red. The orange-red colour is stable for about two minutes. We have also observed that the reaction between oxidised erioglaucine and uranium^{IV} is very rapid, unlike the reaction between ferrin (oxidised ferroïn) and uranium^{IV}. Similar results have been obtained with eriogreen B and xylene cyanol FF. It has also been observed by us that uranium^{IV} salt has no retarding effect on the indicator-ceric sulphate reaction or the oxidised indicator-uranium^{IV} reaction. In the light of these findings, we believe that erioglaucine A, eriogreen B and xylene cyanol FF are particularly suitable for the direct titration of uranium^{IV} with ceric sulphate at the room temperature.The transition at the equivalence point can be taken as yellow to orange-red. The indicator reactions have been observed to be simple, rapid and reversible within a wide range of acidity investigated (0·5 to 8·0*N*). We have found that in titrations with 0·05*N* ceric sulphate, the indicator correction is negligible; an indicator correction of 0·04 ml is necessary with a 0·01*N* solution of ceric sulphate. Of the three dyes tried, we found that erioglaucine A is to be preferred for it gives a more sensitive colour change than the other two. These indicators can also be used with success in hydrochloric acid solution.

Procedure

The following procedure is recommended:—To a known volume of uranium^{IV} solution taken in a conical flask, 0·50 ml of 0·1% erioglaucine solution is added. The solution is diluted and titrated with ceric sulphate with constant stirring. A sharp change of colour from yellow to orange-red indicates the end-point. Some typical values are given in Table I.

TABLE I

Amount of uranium^{IV} taken *m-moles*	Amount of uranium^{IV} found by titration with ceric sulphate *m-moles*		
	with Erioglaucine A as indicator	with Eriogreen B as indicator	with Xylene cyanol FF as indicator
0·0250	0·0252	0·0252	0·0252
0·0500	0·0502	0·0502	0·0504
0·1000	0·1006	0·1004	0·1008
0·3180	0·3188	0·3186	0·3190
0·4488	0·4496	0·4498	0·4498

Similar results have been obtained in the titration of uranium^{IV} with ceric ammonium nitrate in perchloric acid medium, using these dyes as internal indicators. We have found that they cannot be used in the titration of uranium^{IV} with ceric ammonium nitrate in 1·0 to 2·0*N* nitric acid medium. In such titrations, it has been observed that the indicator gives a green-coloured product with the addition of even one or two drops of 0·05*N* ceric ammonium nitrate solution.

The advantages of erioglaucine A, eriogreen B and xylene cyanol FF as indicators in the titration of uranium^{IV}

The preparation of the indicator solution is easy, as the dyes are readily soluble in water and the resulting solutions are stable over a long period. The reaction between the dye and ceric sulphate is quite rapid at the room temperature, as also is the reverse reaction between the oxidised indicator and uranium^{IV}. Titrations of uranium^{IV} are possible with this class of indicators in a wide range of acidity, 0·5*N* to 8·0 *N* H_2SO_4. With the other internal indicators so far investigated, *e.g.* diphenylbenzidine, N-phenylanthranilic acid, and ferroïn, the indicator reactions are not so rapid, and require the use of special conditions of acidity and the use of catalysts like phosphoric acid. These indicators can be used for the titration of uranium^{IV} even with ceric ammonium nitrate in perchloric acid medium (but not in nitric acid medium).

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Züsammenfassung—Es wird der Gebrauch von Triphenylmethanfarbstoffen, Erioglaucin, Eriogrün und Xylenolcyanol FF als innere Indikatoren der cerimetrischen Titration von Uran-IV untersucht. Die Titration ist in der Kälte mit genügender Geschwindigkeit und Genauigkeit möglich, wobei die Farbänderung des Indikators am Äquivalenzpunkt scharf eintritt. Die Reaktionen des Indikators sindschnell und im Aciditätsbereich von 0,5*N* bis 8,0*N* reversibel, im Gegensatz zu anderen schon untersuchtenIndikatoren, z.B. Diphenylbenzidin, N-phenylantranilsäure oder Ferroin, die nur unter genau bestimmten Bedingungen funktionieren-. Man kann auch die Triphenylmethan-Indikatoren bei Titration von Uran-IV mit Ceri-Ammonnitrat in Perchlorsäure, aber nicht in Saltpetersäure benutzen.

Résumé—Les colorants triphénylméthanes, érmoglaucine, ériogreen et xylene cyanole FF ont été utilisés comme indicateurs internes pour le titrage cérimétrique de l'uranium-IV. Le titrage peut s'effectuer à froid avec une rapidité et une précision suffisantes, le virage des indicateurs étant très net au point d'équivalence. Les réactions des indicateurs sont rapides et réversibles dans les limites à d'acidité assez étendues de 0,5*N* à 8,0*N*. D'autres indicateurs examinés, par exemple la diphénylbenzidine, l'acide N-phénylanthranilique et la ferroine, nécessitent, au contraire, pour être efficaces des conditions bien définies. Les indicateurs triphénylméthanes permettent également le titrage de l'uranium-IV avec le nitrate céri-ammoniaque en milieu acide perchlorique (non pas en milieu acide nitrique).

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ON THE INDUCED REDUCTION OF CHLORATE IONS

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Summary—The induced reduction of chlorate ions can be carried out only by 1-equivalent oxidising agents. As^{IV} is formed by these, and this reduces chlorate very rapidly. The properties and mechanism of the induced reduction are discussed in detail.

For the determination of chlorate ions a reliable method is given, based on this induced reduction.

IT is well known that the reaction between chloric acid and arsenious oxide is very slow, but with the aid of osmium tetroxide the reaction can be accelerated very markedly.[1] However, the catalysed reaction is not sufficiently rapid for a direct titration of chlorate ion. According to Gleu[2] the determination can be carried out only by adding arsenious acid in excess and back-titrating with ceric sulphate or potassium permanganate. During the back-titration an induced reaction takes place resulting in the instantaneous reduction of chlorate ions.

The analytical features of the reduction of chlorate were discussed in Gleu's work exhaustively, but no information about the mechanism of induced reaction was obtained. The present paper deals mainly with the mechanism of induced chlorate reduction.

EXPERIMENTAL

Reagents

$0{\cdot}1N$ arsenious acid, $0{\cdot}1N$ cerium^{IV} sulphate, $0{\cdot}1N$ potassium permanganate and $0{\cdot}1N$ potassium dichromate solutions were prepared from c.p. substances and standardised in the customary way. $0{\cdot}1N$ cobalt^{III} sulphate solution was prepared by electrolytic oxidation according to Swann and Xanthakos:[3] $0{\cdot}1N$ manganese^{III} sulphate solution by oxidation of manganese^{II} sulphate with permanganate: the stock solution of $0{\cdot}1N$ ($M/60$) potassium chlorate was prepared by dissolving Merck c.p. material: $0{\cdot}01M$ osmium tetroxide in $0{\cdot}1N$ sulphuric acid: 0·025 Ferroïn indicator solution.

Procedure

10·0 and 20·0 ml of $0{\cdot}1N$ arsenious acid solution, respectively, were acidified with an adequate quantity of 20% sulphuric acid, and 5·0 and 10·0 ml of $0{\cdot}1N$ potassium chlorate solution, respectively, were added. After adding 2 drops of osmium tetroxide as catalyst the excess of arsenious acid was titrated with one of the abovementioned oxidising standard solutions.

1. *The rate of reaction between arsenious acid and chlorate ions in presence of osmium tetroxide*

The effectiveness of OsO_4 catalyst was tested as follows: To samples consisting of 10 ml $0{\cdot}1N$ As_2O_3 + 4·96 ml $0{\cdot}1N$ $KClO_3$ + 5 ml 20% H_2SO_4 and 2 drops of $0{\cdot}01M$ OsO_4, after varying times, 5 ml $0{\cdot}1M$ H_2O_2 solution was added. The excess of arsenious acid was thus oxidised to arsenate instantaneously, and the reduction of chlorate was stopped. After this 5·0 ml $0{\cdot}1N$ $AgNO_3$ was pipetted into the solution and the excess measured with $0{\cdot}1N$ KCl solution potentiometrically. Since in acidic solution osmium tetroxide decomposes hydrogen peroxide very slowly, after the titration of the silver ions the hydrogen peroxide remaining could also be determined. The extent of reduction of chlorate ions was determined, on the one hand, by titrating the chloride ions formed, and, on the other hand, by determination of the excess of the arsenious acid. Their mean values are summarised in Table I. From the data it can be seen that the catalysed reduction of chlorate is not complete even after 6 hours.

This reaction being too slow for direct determination can be accelerated by an induced reaction so as to take place instantaneously.

Table I. Rate of reaction between arsenious acid and chlorate catalysed by osmium tetroxide

Waiting time *min*	0·1*N* $KClO_3$, *ml*		Reduction of chlorate %
	Taken	Found	
2	4·96	3·55	71·5
5	4·96	4·11	82·8
10	4·96	4·32	87·0
30	4·96	4·54	91·5
60	4·96	4·70	94·5
360	4·96	4·95	99·5

Table II. Titrant, 0·1*N* cerium^{IV} sulphate

Initial volume	20% H_2SO_4 *ml*	Duration of titration *sec*	0·1*N* $KClO_3$, *ml*		Difference *ml*
			Taken	Found	
50	0·5	40	9·92	10·21	0·29
50	1·0	39	9·92	10·18	0·26
50	0·5	40	9·92	10·10	0·18
50	10·0	38	9·92	10·06	0·14
50	20·0	43	9·92	10·00	0·08
50	20·0	30	9·92	9·95	0·03
50	20·0	41	9·92	9·99	0·07
50	20·0	103	9·92	10·05	0·13
50	20·0	124	9·92	10·07	0·15
50	20·0	194	9·92	10·12	0·20
50	20·0	40	9·92	9·98	0·06
100	40·0	40	9·92	10·53	0·61
200	80·0	38	9·92	10·73	0·81
300	120·0	40	9·92	11·06	1·17

Samples were deaerated by 1 g $KHCO_3$ before adding OsO_4.

2. *Titration with cerium^{IV} sulphate solution*

Measurements carried out by cerium^{IV} sulphate titration have supported Gleu's observation completely. The reduction of chlorate ions is accompanied by rapid air-oxidation, causing a considerable positive error in the amount of chlorate obtained. The magnitude of this error depends markedly on the concentration of acid and on the speed of the titration as well as on the volume of the titrated solution. The results in Table II show that on increasing the acid concentration the error is decreased; on adding 20 ml of 20% sulphuric acid (in 50 ml volume) it is less than 1%. On increasing the speed of titration the error becomes also smaller. Titrating the solution very rapidly (30 sec) the error is no longer considerable. Increasing the volume of the sample (keeping the acid concentration of the solution constant) the error increased proportionally, showing that the 1 g added $KHCO_3$ is not sufficient for the de-aeration of the larger volume.

It is known that during the reaction between arsenious acid and cerium^{IV}-sulphate air oxidation does not occur. Therefore we must examine how the reaction between arsenious acid and oxygen can take place coupled with the reduction of the chlorate ions. To a solution of the composition: 5 ml 0·1*N* $KClO_3$ + 5 ml 20% H_2SO_4 + 10 ml 0·1*N* As_2O_3 + 20 ml water, 2 drops of osmic acid catalyst were added and after exactly 120 sec the excess of arsenious acid was determined with cerium^{IV} sulphate. The time of titration was 75 sec. A positive error of 0·6 ml (12%) was found. (Table III, Experiments 1, 2, 3). When after 120 sec the absorbed oxygen was expelled from the solution by means of 2 g $KHCO_3$ (experiments 4, 5, 6) the error decreases to about one-third. On the contrary, when the solution was deaerated at the beginning, an error of only 0·2% was found (experiments 7, 8 and 9). The oxidation of the arsenious acid by atmospheric oxygen must therefore take place in the course of the reaction between arsenious acid and chlorate catalysed by OsO_4 as well as in that induced by cerium^{IV}-sulphate.

TABLE III. TITRANT, 0·1*N* CERIUM^{IV} SULPHATE

No.	$KHCO_3$ *g*		0·1*N* $KClO_3$, *ml*		Difference *ml*
	A	B	Taken	Found	
1	—	—	4·96	5·58	0·62
2	—	—	4·96	5·55	0·59
3	—	—	4·96	5·53	0·57
4	2	—	4·96	5·14	0·18
5	2	—	4·96	5·13	0·17
6	2	—	4·96	5·14	0·18
7	—	2	4·96	4·96	0·0
8	—	2	4·96	4·96	0·0
9	—	2	4·96	4·97	0·01

A: $KHCO_3$ applied 120 sec after adding the catalyst.
B: $KHCO_3$ added at the beginning.

Recently the determination of chlorate ions in the presence of a large amount of perchloric acid has been carried out by Smith and Veraguth[4] according to Gleu's procedure and no oxidation by atmospheric oxygen was observed at all. Checking this observation, it was found that perchlorate ions are completely inactive, but that the presence of large amounts of perchloric acid (due to the great hydrogen ion concentration) markedly decreases air-oxidation. However, in the presence of 1·0*N* acid a considerable positive error was still observed.

During the induced reduction of chlorate a strong smell of chlorine dioxide was observed and in the initial stage of titration the solution also remains weakly yellow in colour after the reduction of cerium^{IV} ions. In the course of the catalysed reaction between chlorate ions and arsenious acid the formation of chlorine dioxide is also observed, but its amount is very small compared with that formed during the induced reduction.

Halide ions inhibit the induced reduction of chlorate ions. An equivalent effect is exerted by 0·05 ml of 0·1*N* KI, 2·0 ml of 0·1*N* KBr and 20 ml of 0·1*N* KCl. The order of effectiveness is therefore $I^- > Br^- > Cl^-$ (at about 400 : 10 : 1). This agrees with the order observed in the catalysis of the reaction between arsenious acid and cerium^{IV} sulphate.[5]

3. *Titration with potassium permanganate*

The induced reduction of chlorate can also be carried out by titrating it with potassium permanganate. A striking difference in comparison with the titration with cerium^{IV} sulphate is that the induced reduction is considerably slower. Quantitative reduction of chlorate ions is not attained, by rapid titration (Table IV, Column A) while in the determinations with cerium^{IV} sulphate the reduction is complete even in the case of a more rapid titration (Table II.).

Recently we have observed[6] that the difference between the reactions of cerium^{IV} sulphate and permanganate is chiefly due to the fact that the Ferroïn indicator acts as a catalyst, and accelerates the reaction of cerium^{IV} ions. Consequently experiments were carried out to determine whether the difference in the rate of the reduction of the chlorate is caused by the catalytic characteristics of the Ferroïn. As can be seen from Table IV, column B, Ferroïn accelerates the reduction of chlorate but there still remains an additional difference between the titrations carried out with permanganate and cerium^{IV} sulphate.

TABLE IV. TITRANT, 0·1*N* POTASSIUM PERMANGANATE

Duration of titration *sec*	$0{\cdot}1N$ $KClO_3$, *ml*			Difference, *ml*	
	Taken	Found			
		A	B	A	B
42	9·92	9·35	9·87	−0·57	−0·11
73	9·92	9·84	9·96	−0·08	+0·04
90	9·92	10·17	10·17	+0·25	+0·25
170	9·92	10·27	10·34	+0·35	+0·42

A: without Ferroïn indicator.
B: in presence of 1 drop 0·025*M* Ferroïn solution.

Otherwise the characteristics of the titration with permanganate agree qualitatively very well with those of the titration with cerium^{IV} sulphate. Strong air oxidation also takes place and this depends in the same way on the experimental conditions.

4. *Titrations by means of* Br_2, $KBrO_3$, Cl_2, KIO_4 *cobalt*^{III} *and manganese*^{III} *sulphate solutions*

Using Br_2 or $KBrO_3$ solutions, for the back-titration of the excess arsenious acid, reduction of chlorate takes place only to an extent of 70%. This fact is in good agreement with the results in Table I. On this basis it may be concluded that the reaction of arsenious acid with Br_2 or with $KBrO_3$, cannot induce the reduction of chlorate ions.

Similarly when the back-titration of the arsenious acid is carried out with Cl_2 or KIO_4 solutions, the chlorate reduction is only 70%. Since each of these reagents oxidises in 2-equivalent steps, it appears that *the induced reduction of chlorate ions cannot take place with 2-equivalent reagents.*

Cerium^{IV} sulphate, which is very effective, always oxidises with 1-equivalent; potassium permanganate can also react in 1-equivalent steps. Thus it is possible that the induced reduction of chlorate ions can be carried out by means of other 1-equivalent reagents. To examine this, titrations with cobalt^{III}, manganese^{III} sulphate and dichromate solutions were carried out.

From the results summarised in Table V, it is apparent that the cobalt^{III} and manganese^{III} ions behave as very strong inducing agents. Quantitative chlorate reduction is attainable when arsenious acid is used in only 20% excess. In the case of both reagents, but particularly with manganese^{III} sulphate, strong chlorine dioxide evolution can be observed. The inducing effect of potassium dichromate (which also can oxidise with 1-equivalent) was found very poor.

Finally it was found that silver^{I} ions accelerate the reduction of chlorate ions. When to a solution containing chlorate and arsenious acid, in which silver nitrate is present, osmium tetroxide is added, sudden precipitation of AgCl is observed. In the presence of silver ions, in 2 minutes, chlorate ions were reduced to an extent of about 90%, while without silver the reduction is only about 70%. A few seconds after the addition of osmium tetroxide the precipitate becomes brownish. This tint completely disappears during 30–40 sec and the solution becomes milk-white due to the silver chloride formed.

It is worth noting that in the presence of silver^{I} ions the oxidation of arsenious acid by atmospheric oxygen decreases considerably (Table VII).

Table V

	0·1N As_2O_3 *ml*	0·1N $KClO_3$, *ml*		Difference *ml*
		Taken	Found	
A	20·00	9·92	10·12	+0·20
	15·00	9·92	10·06	+0·14
	12·00	9·92	10·05	+0·13
	20·00	9·92	9·90*	−0·02
B	20·00	9·92	10·46	+0·54
	15·00	9·92	10·23	+0·31
	12·00	9·92	10·13	+0·21
	20·00	9·92	9·94*	+0·01

A: Titrant, 0·1N $Mn_2(SO_4)_3$. B: Titrant, 0·1N $Co_2(SO_4)_3$.
* Oxygen expelled before measurement by means of $KHCO_3$.

Table VI. Titrant, 0·1N potassium dichromate

Waiting time *min*	0·1N $KClO_3$, *ml*		Reduction of chlorate %
	Taken	Found	
2	9·92	8·69	87·5
5	9·92	9·33	94·0
10	9·92	9·65	97·2
60	9·92	9·90	99·7

Since the rate of reaction between arsenious acid and potassium dichromate under the experimental conditions is not sufficiently rapid for a direct titration, the reaction between chlorate and arsenious acid was stopped after the given waiting time by adding potassium dichromate in excess and back-titration potentiometrically with arsenious acid.

Table VII. Titrant 0·1N cerium^{IV} sulphate

0·1N $AgNO_3$ *ml*	$KHCO_3$, *g*		0·1N $KClO_3$, *ml*		Difference *ml*
	A	B	Taken	Found	
—	—	—	4·96	5·55	+0·59
—	—	2	4·96	4·96	0·0
5	—	—	4·96	5·11	+0·15
5	—	—	4·96	5·10	+0·14
5	—	—	4·96	5·11	+0·15
5	2	—	4·96	5·07	+0·11
5	2	—	4·96	5·08	+0·12
5	2	—	4·96	5·06	+0·10
5	—	2	4·96	4·96	0·0
5	—	2	4·96	4·98	+0·02
5	—	2	4·96	4·95	−0·01

A: $KHCO_3$ added 2 min after OsO_4. B: $KHCO_3$ added before OsO_4 catalyst.

DISCUSSION

The reaction between arsenious acid and chlorate ions has been found to be bimolecular by Stefanovskii and Zan'ko.[7]

$$HClO_3 + As^{III} \rightarrow HClO_3^- + As^{IV}$$

This equation offers an adequate explanation of the observations by Rutter[8] and by McDougall,[9] that during the reaction chlorine dioxide forms. Alternatively arsenious acid may reduce the chlorate to chlorite, the chlorous acid then giving chlorine dioxide in a rapid reaction:

$$HClO_2 + HClO_3 \rightarrow 2ClO_2 + H_2O$$

The formation of As^{IV} during the reaction between the chlorate ions and arsenious acid on the basis of Gleu's observation must be considered to be possible. Gleu[10] found that during the reaction between arsenious acid and chlorate catalysed by osmium tetroxide, vanadate is reduced to vanadium^{IV}. As arsenious acid cannot reduce vanadate even in the presence of osmium tetroxide, it is reasonable to suppose that the inducing reaction produces As^{IV}, which is more effective than As^{III}.

To elucidate the mechanism of the induced reduction of the chlorate the inducing reaction between cerium^{IV} and arsenious acid must be examined. According to Stefanovskii[11] the rate-determining step of this reaction is bimolecular, and arsenite will be oxidised to AsO_2. Recently the cerium^{IV} arsenious acid reaction was re-investigated by Moore and Anderson,[12] who found that within a small range of concentration (0·0122–0·0230 mol/l cerium^{IV}) the reaction is 3rd order. Although the values of the termolecular rate constant vary considerably on changing the experimental conditions (*e.g.* with change of concentration) yet according to Moore and Anderson the postulation of the formation of As^{IV} is not permissible.

Although kinetic data do not furnish a satisfactory decision, we are of the opinion that to postulate the formation of As^{IV} is justified, because of the inducing effect of the reaction mentioned. The results obtained prove unequivocally that inducing effects are shown only by 1-equivalent reagents, while 2-equivalent reagents are inactive. The production of As^{IV} is also supported by the observation that during the inducing reaction chlorine dioxide is evolved in considerable quantity. Evolution of chlorine dioxide is also observed in every case where chlorate is attacked with 1-equivalent reducing agents (*e.g.* with vanadium^{III}).

In our opinion during the inducing reaction the As^{IV} formed reduces the chlorate very rapidly to chlorine dioxide. The chlorine dioxide reacts with arsenious acid relatively slowly and according to Bray[13] chlorite ions forms. During this latter reaction As^{IV} formed reduces the chlorite to ClO, from which finally chloride will be obtained.

It was mentioned that halide ions inhibit the induced reduction of chlorate. This effect can be explained by a change in the mechanism of the reaction between cerium^{IV} and arsenious acid: that is, that the ceric ions oxidise the iodide, bromide and chloride ions into iodine, bromine and chlorine; the free halogens then convert arsenite into arsenate directly and rapidly. Therefore the presence of halide ions decreases and (when a suitable quantity is present) exclude the formation of As^{IV}. Consequently the induced reduction of chlorate ions decreases or is prevented.

During the induced reduction of chlorate, strong oxidation by atmospheric oxygen can be observed. On the contrary, in the course of the reaction between arsenious acid and cerium^{IV} there is no oxidation by air. Therefore it appears that As^{IV} is not a sufficiently strong reducing agent to attack molecular oxygen. Considering the behaviour of As^{IV} in the induced reduction, it can be said that the standard oxidation potential of the As^{IV}/As^{V} couple is about 0·3–0·4 V. By analogy with the corresponding couples of antimony the same value can be deduced.

As As^{IV} is inert from the point of view of the reaction with the O_2 molecule, one of the reduction products of the chlorate ion must be responsible for the observed strong oxidation by air. This is supported by the fact that the oxidation by air, *i.e.* the extent of the positive error, is proportional to the progress of the induced reduction.

Chlorate, chlorine dioxide and chlorite ions are inactive toward atmospheric oxygen, while the ClO radical easily reacts with oxygen, according to the reaction

$$ClO + O_2 \rightleftharpoons ClO_3$$

which is about thermoneutral (Szabó[14]). The ClO_3 formed in all probability can be reduced more easily than chlorate.

In our opinion the effect of silver salts is to accelerate the reduction of chlorite ions to chloride. In consequence of this catalysis, there is only a very small amount of ClO, or none, formed from the chlorite. In the absence of oxygen-carrying substance, due to the presence of silver ions, the oxidation by atmospheric oxygen must be ruled out.

Our conception of the induced reduction of chlorate may be summarised in the following scheme:

Inducing reaction:

$$Ce^{IV} + As^{III} \rightarrow Ce^{III} + As^{IV}$$

Induced reactions:

(1) $$HClO_3 + As^{IV} \rightarrow As^{V} + HClO_3^- \rightleftharpoons ClO_2 + OH^-$$

(2) $$ClO_2 + As^{III} \rightarrow As^{IV} + ClO_2^-$$

(3) $$HClO_2 + As^{IV} \rightarrow As^{V} + HClO_2^- \rightleftharpoons ClO + OH^-$$

(4) $$2\,ClO + 4H^+ + 3As^{III} \rightarrow 2Cl^- + 2H_2O + 3As^{V}$$

Induced oxidation by air:

$$ClO + O_2 \rightleftharpoons ClO_3$$

$$ClO_3 + 6H^+ + 3As^{III} \rightarrow Cl^- + 3As^{V} + 3H_2O$$

Finally, the accelerating and inhibiting effect of silver ions can be applied to the determination of chlorate ions to obtain more accurate data. For the titration of the chlorate ions the following procedure is recommended:

Acidify the sample containing 3–35 mg chlorate with 10–20 ml of 20% sulphuric acid, add 5–10 ml 0·1*N* silver nitrate and dilute the solution to 50–60 ml. After de-aerating the solution by means of 1–2 g $KHCO_3$, add arsenious acid in excess and 2 drops of 0·01*M* OsO_4 as a catalyst. After 1–2 min back-titrate the arsenious acid with standard cerium^{IV} sulphate solution.

Errors are as small as 0·1%.

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Zusammenfassung—Man kann die induzierte Reaktion von Chlorat-Ionen nur mittels 1-Äquivalent-Oxydiermittel durchführen. Mit diesen Substanzen wird Arsen(IV) gebildet, und dies reduziert Chlorat sehr rasch. Die Eigenschaften und Mechanik der induzierten Reaktion werden umständlich erörter. Zur Bestimmung von Chlorat-Ionen wird eine zuverlässige auf dieser induzierten Reduktion basierte Methode gegeben.

Résumé—La reaction induite des ions chlorates ne s'effectue qu'en présence des oxydants "l-équivalent". Au moyen de ces réactifs on obtient l'arsenic-IV qui réduit très rapidement les ions chlorates. On discute en détail les propriétés et la mechanisme de la réaction induite.

On décrit une méthode sûre de dosage des ions chlorates basée sur cette réaction induite.

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SPOT TEST DETECTION OF PHENYLHYDRAZINE AND ARSONIC ACIDS*

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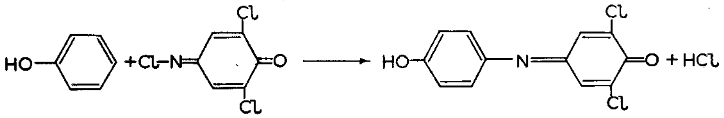
Summary—If phenylhydrazine or its salts are heated with arsenic acid or with one of its organic derivatives (aliphatic or aromatic arsonic acids) phenol results. The latter can easily be detected in the gas phase by the indophenol reaction with 2:6-dichloroquinone-4-chloroimine. This has been made the basis of characteristic tests for phenylhydrazine (also phenylhydrazones and osazones) as well as for arsonic acids. When conducted within the bounds of spot test analysis, the limits of detection are microanalytical.

IT has been shown elsewhere[1] that the indophenol reaction of phenols with 2 : 6-dichloroquinone-4-chloroimine[2] discovered by Gibbs[3] may be employed in spot test analysis for the detection of volatile phenols or of phenols that are being carried along by water vapour. The condensation



can be accomplished for analytical purposes by allowing the phenol vapours to come into contact with filter paper which has been impregnated with the reagent by bathing the paper in a saturated benzene solution of the imine. Phenols produce a brown-yellow to light yellow stain on the reagent paper and on exposure to ammonia vapour the stain turns blue because of the formation of the ammonium salt of the indophenol. This colour reaction will reveal as little as 0·3 μg of carbolic acid.

The procedure provides a reliable preliminary test for aromatic compounds which contain oxygen in the nucleus or in a side chain, since such compounds almost invariably yield phenols on pyrolysis. (Certain azo dyes containing phenolic OH groups do not follow this rule.) Furthermore, it was possible to work out tests[1] for phenyl esters and phenyl ethers which were based on the finding that these compounds yield phenols through pyrohydrolysis or dealkylation at 150°. The pyrohydrolysis[2] is accomplished by heating the sample with oxalic acid dihydrate; the dealkylation ensues if the compound is heated with a mixture of potassium iodide and oxalic acid dihydrate. All of these tests can be successfully conducted within the bounds of spot test analysis.

This paper describes two additional tests in this category, based on the production of phenol.

It has long been known[4] that phenylhydrazine is oxidatively decomposed even at room temperature by arsenic acid:

$$C_6H_5NH\,NH_2 + 2H_3AsO_4 \rightarrow 2H_3AsO_3 + N_2 + H_2O + C_6H_5OH$$

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* Translated by R. E. Oesper, University of Cincinnati, U.S.A.

If this redox reaction is conducted at 100°, the phenol is carried along with the water vapour and gives the indophenol reaction in the gas phase. An excellent test for phenylhydrazine has been constructed on this finding and the test may be extended to its condensation products with aldehydes and ketones.

It has furthermore been found that aliphatic and aromatic arsonic acids resemble their parent acid in the ability to oxidize phenylhydrazine to produce phenol. Consequently, a reliable test for arsonic acids has resulted.

I. DETECTION OF PHENYLHYDRAZINE

Procedure: One drop of the test solution is mixed in a micro test tube with a drop of concentrated arsenic acid solution. The mouth of the tube is covered with a disc of filter paper impregnated with a saturated benzene solution of 2:6-dichloroquinone-4-chloroimine and placed in a boiling water bath for 3–4 minutes. In the presence of phenylhydrazine a pale brown stain appears on the paper and turns blue when held over ammonia vapour. The blue colour is not permanent, but it can be restored by again exposing the reagent paper to ammonia vapour.

Limit of detection: 5 μg phenylhydrazine.

Phenylhydrazones and phenylosazones can likewise be detected by the above procedure.

A preliminary separation is essential if phenols are present. This is readily accomplished by shaking the alkaline test solution with an organic liquid which is immiscible with water (ether, benzene, etc.). The phenolate remains in the water layer.

II. DETECTION OF ARSONIC ACIDS

Procedure: A little of the solid or 1 drop of its aqueous solution is placed in a micro test tube along with an additional drop of water and several cg of phenylhydrazine hydrochloride. The mouth of the test tube is covered with a disc of filter paper that has been bathed in a saturated benzene solution of 2:6-dichloroquinone-4-chloroimine. The tube is kept in a boiling water bath for about 5 minutes. The paper is then exposed to strong ammonia vapour. A positive response is indicated by the development of a blue stain.

The procedure revealed:

5 μg *p*-aminophenylarsonic acid
5 μg *p*-hydroxyphenylarsonic acid
10 μg *p*-dimethylamino-azo-phenylarsonic acid

Zusammenfassung—Bei Erwärmung von Phenylhydrazin und dessen Salzen mit Arsensäure oder deren organischen Derivaten (aliphatische und aromatische Arsonsäeuren) entsteht Carbolsäeure, die in der Gasphase durch die Indophenolreaktion mit 2,6-dichloroquinone-4-chlor-imin empfindlich nachweisbar ist. Dies ermöglicht charakteristische Nachweise von Phenylhydrazin (auch Phenylhydrazone und Ozazone), sowie von Arsonsäuren, die in der Technik der Tüpfelanalyse ausgeführt mikroanalytische Erfassungsgrenzen besitzen.

Résumé—En chauffant la phénylhydrazine ou ses sels avec de l'acide arsénique ou avec un de ses dérivés organiques (acides arsoniques aliphatiques ou aromatiques) on obtient du phénol. On peut facilement déceler en phase gazeuse ce dernier comme indophénol par réaction avec la 2:6-dichloroquinone-4-chloroimine. On a également utilisé cette réaction comme base des essais caractéristiques pour la phénylhydrazine (et pour les phénylhydrazones et les osazones) ainsi que pour les acides arsoniques. Lorsque l'on opère dans les conditions de l'analyse à la touche les limites de détection sont microanalytiques.

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DETERMINATION OF VANADIUM IN HIGH ALLOY STEELS BY ISOTOPE-DILUTION

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(*Received* 7 *July* 1958)

Summary—An isotope-dilution method has been developed for the determination of vanadium in high-alloy steels. Vanadium is titrated amperometrically after removal of chromium as chromyl chloride. Vanadium losses due to adsorption were corrected for radiometrically. The procedure was tested on N.B.S. steel samples and showed good precision and accuracy.

In the analysis of tungsten-containing high alloy steels, vanadium, among other elements, is adsorbed on the precipitate of tungstic acid that is formed during solution of the sample. For accurate results it would therefore be necessary to analyse the precipitate as well as the solution for vanadium content. An isotope-dilution procedure, however, readily permits a correction for vanadium losses in the precipitate to be made. As a gravimetric determination is rather impracticable, an amperometric procedure has been used for the determination of the vanadium content of the solution.

Choice of method

As an amperometric titration is sensitive as well as accurate, this method was chosen for the determination of vanadium. The procedure adopted has been studied by Parks and Agazzi[1] and by Rulfs and coworkers.[2]

V^V is titrated with Fe^{II} after first being oxidised by means of $KMnO_4$ in slight excess. Parks and Agazzi destroy the excess of permanganate by means of NaN_3, whereas Rulfs uses $NaNO_2$-urea. From results on pure vanadium solutions in perchloric acid medium it appears that $NaNO_2$-urea is to be preferred, as NaN_3 often gives rise to intermediate manganese oxides which are reduced only with difficulty.

EXPERIMENTAL

Apparatus

Micro-platinum anode, 5 mm long, wire gauge 25, driven by a synchronous motor at 360 rpm.

Standard Calomel Electrode as reference connected through a 3% $(NH_4)_2SO_4$ bridge to the solution to avoid interference of chloride ions.

Kipp No. A70 galvanometer.

Tracerlab Superscaler and P20–A well-type NaI(Tl) detector.

5-ml microburette.

Reagents

0·01*N* ferrous ammonium sulphate stock solution in 2% H_2SO_4, standardised against $K_2Cr_2O_7$. The normality of this solution is kept constant by inserting an aluminium wire in the stock solution.[3]

0·01*N* NH_4VO_3 stock solution in 2% H_2SO_4 standardised by potentiometry and amperometry against ferrous ammonium sulphate solution. Before titration the vanadium is oxidised with $KMnO_4$, as the solution is slowly reduced to the V^{IV} state.

Amperometric titration

In a series of determinations made on pure vanadium solutions, accurate results were obtained using a polarising voltage of 0·85 volts measured against the S.C.E. For vanadium solutions containing 4 μ equivalents/50 ml to 40 μ equivalents/50 ml the mean deviation was better than 0·45 %, the accuracy always being better than 1 %.

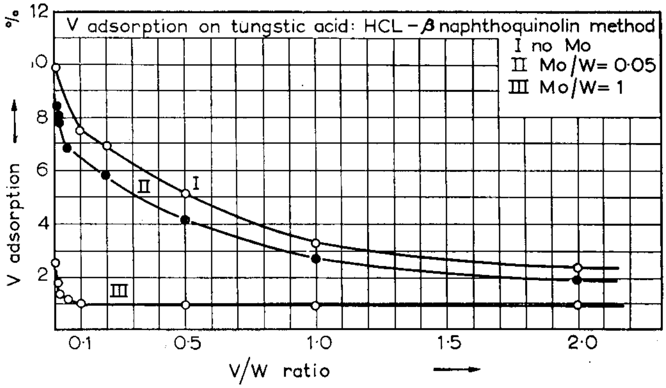

FIG. 1.

Tracer vanadium

Carrier-free ^{48}V ($t_{\frac{1}{2}}$ = 16·2*d*; β^+ : 0·69; γ : 0·99, 1·32, 2·23 MeV) was used as a tracer. This isotope was prepared by the bombardment of a titanium target with 12-MeV deuterons in the Louvain cyclotron. The procedure for the carrier-free separation of ^{48}V has already been described.[4] A modification of this procedure using di-*iso*butyl ketone will be reported in detail elsewhere.

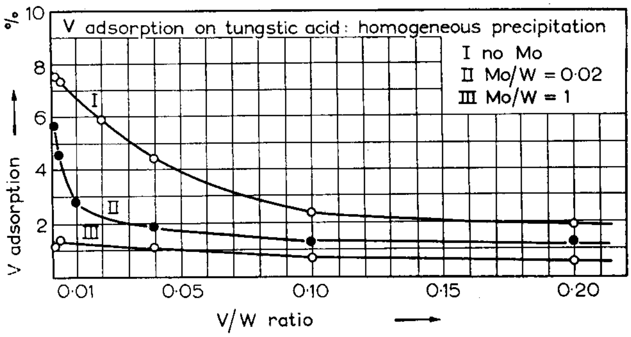

FIG. 2.

Vanadium adsorption on tungstic acid

Tracer vanadium was used to study the importance of the adsorption on the tungstic acid precipitate. The tungstic acid was precipitated by the method of Claeys[5] with β-naphthoquinoline, as this reagent is preferable to the generally used cinchonine. In these experiments 100 mg tungsten (as tungstate) were used, to which increasing amounts of vanadium carrier were added as well as a constant activity of carrier-free ^{48}V. The results are summarized in Fig. 1. It appears that the vanadium adsorption is closely dependent on the vanadium-molybdenum ratio, as well as on the vanadium-tungsten ratio. A high molybdenum content to reduce the vanadium adsorption.

As the presence of organic material is to be avoided in the subsequent titration of vanadium, and since a quantitative precipitation of tungsten is not required, the adsorption of vanadium on tungsten was also studied using perchloric acid in the presence of hydrogen peroxide on 100-mg amounts of tungsten. In this case a solution of pertungstate is obtained which slowly decomposes on heating and causes homogeneous precipitation of tungstic acid. As can be seen from Fig. 2, vanadium adsorption is considerably reduced but is still quite important. Accurate results can therefore not be obtained if the solution only is analysed for vanadium content.

Interference of chromium

From amperometric titrations of synthetic samples, it appeared that large amounts of chromium interfere. For a Cr/V ratio of 250 for instance, the results are too high by 6%. This is obviously due to a partial oxidation of Cr^{III} to Cr^{VI} by the excess permanganate. Chromium was therefore separated as CrO_2Cl_2 before the titration. This can easily be achieved quantitatively by passing *dry* HCl into the hot perchloric acid solution. The use of dry HCl is necessary, as aqueous HCl causes reduction of Cr^{VI} to Cr^{III}. Tracer experiments with ^{51}Cr showed that the removal was quantitative after 10 minutes.

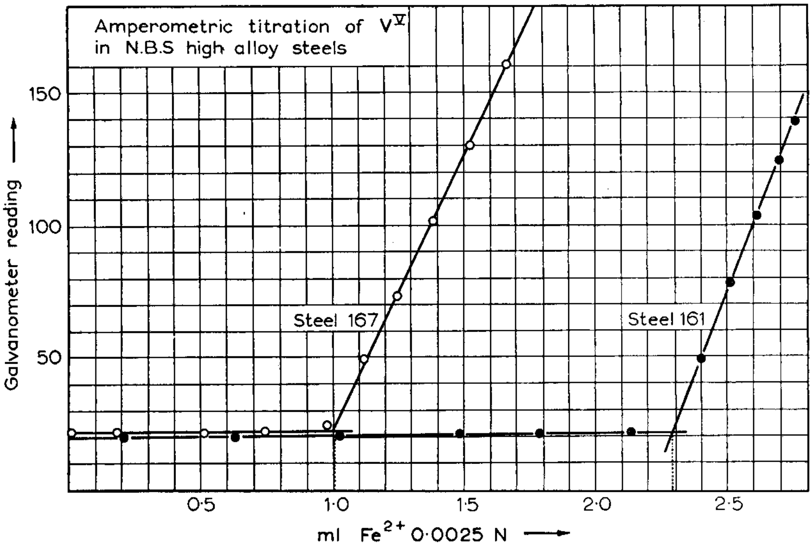

FIG. 3.

Procedure

0·1 to 1 g of steel turnings is dissolved in 30 ml of concentrated HCl. After the reaction has subsided 20 ml of HNO_3 ($d = 1·40$) are added and the solution is evaporated on a hot plate. 30 ml of $HClO_4$ are added to the residue and the solution is taken to fumes, eliminating HCl and HNO_3. The solution and the precipitate are transferred quantitatively into a platinum dish together with 4 ml HF, and a suitable amount of carrier-free ^{48}V is added (about 500,000 counts/min). The precipitate, consisting mainly of hydrates of SiO_2, WO_3, Nb_2O_5, Ta_2O_5, TiO_2 and adsorbed elements, goes into solution on heating. The solution is taken to fumes again, driving out HF as well as SiF_4, and causing precipitation of the insoluble acids. After dilution with approximately 20 ml of water, the solution is filtered into a 250-ml beaker through an asbestos filter and again evaporated to fumes of $HClO_4$ on a hot plate. 20 Ml of $HClO_4$ are added and *dry* HCl gas is passed through the boiling solution for about 10 minutes eliminating chromium as brown fumes of CrO_2Cl_2. After the removal of the chromium, boiling is continued to remove HCl and the solution is finally diluted with water to approximately 50 ml. A few drops of 1% ferrous sulphate in 2% H_2SO_4 are added to reduce vanadium to V^{IV}. 0·05N $KMnO_4$ is then added in just enough excess to give a slightly pink colour. The excess $KMnO_4$ is destroyed after standing 5 minutes at 20° by adding 2–3 drops of 2% $NaNO_2$ followed by 500 mg of urea. Vanadium is then titrated amperometrically with *ferrous sulphate* added from a micro-burette. (The normality of the ferrous sulphate solution varied from 0·0025N to 0·025N depending on the vanadium content of the sample.) The rotating Pt electrode should not be introduced into the solution before the removal of the excess $KMnO_4$. A typical titration is represented in Fig. 3.

After the titration the solution is partially evaporated, transferred to a 50-ml graduated flask and diluted to the mark. 4 Ml of this solution are counted in the well-type detector.

TABLE I. DETERMINATION OF V IN HIGH-ALLOY STEELS

NBS steel	NBS results		Isotopic dilution analysis		
	mean value $\overline{m}$	mean error $\overline{\Delta}$	%V found	mean value $\overline{m}$	mean error $\overline{\Delta}$
132$_{\text{A}}$[a]	1·94%	0·009%	1·931	1·93^1%	0·008%
			1·940		
			1·942		
			1·928		
			1·913		
153[b]	2·04	0·022	2·02^4	2·04^7	0·02^6
			2·07^8		
			2·04^7		
			2·08^1		
			2·00^7		
123$_{\text{B}}$[c]	0·05 provis. certif.		0·054	0·053	0·001
			0·052^3		
			0·055		
			0·055		
			0·053		
101$_{\text{D}}$[d]	0·049	0·0022	0.049^1	0·048^8	0·0007
			0·047^4		
			0·048^3		
			0·049		
			0·050		
161[e]	0·029	0·005	0·030^6	0·030^7	0·000^3
			0·030^6		
			0·031^1		
			0·031^1		
			0·030^1		
167[f]	0·01 provis. certif.		0·0080^7	0·0080^7	0·0000^9
			0·0082^6		
			0·0080		
			0·0079^6		

Composition in % according to N.B.S. certification

[a] Mn 0·268; Ni 0·137; Cr 4·21; Mo 4·51; W 6·20
[b] Mn 0·219; Ni 0·107; Cr 4·14; Co 8·45; Mo 8·39; W 1·58
[c] Mo 0·17; W 0·18; Ta 0·20; Nb 0·75
[d] Mn 0·39; Ni 9·05; Cr 18·68; Co 0·058; Mo 0·11
[e] Mn 1·28; Ni 64·3; Cr 16·9; Co 0·47; Mo 0·005
[f] Mn 1·64; Ni 20·65; Cr 20·00; Co 42·9; Mo 3·90; W 4·50; Ta 0·08; Nb 3·75.

Calculation of the results

The V content of the sample is given by:

$$\%\text{V} = \frac{50{\cdot}95}{10\,.\,a}\left[\frac{v\,.\,t}{1-\alpha}\right]$$

where t = normality of the ferrous solution,
a = sample weight in g,
v = volume in ml of ferrous sulphate,

$$1-\alpha = \frac{A_x \cdot 50}{A_{\text{tot}} \cdot 4} = \text{fractional vanadium yield:}$$

A_{tot} = total activity of ^{48}V added:
A_x = activity of ^{48}V in the 4-ml sample.

TABLE II. DETAILED SURVEY OF THE ISOTOPE-DILUTION ANALYSIS OF NBS STEEL 167

a_g	$^{v}\mathrm{Fe}^{\mathrm{II}}$, *ml*	% V uncorrected	$(1 - \alpha)$	% V corrected	NBS results
2000·2	1·003	0·0064^9	0·804	0·0080^7	0·01 provis. certif.
2009·5	1·026	0·0065^9	0·800	0·0082^6	
2000·2	1·023	0·0066^0	0·827	0·0080^0	
2000·1	0·881	0·0057^0	0·716	0·0079^6	
		$\overline{m}$ = 0·0063^5 $\overline{\Delta}$ = 0·0003^2		$\overline{m}$ = 0·0080^7 $\overline{\Delta}$ = 0·0000^9	

RESULTS

The procedure described was tested on a number of U.S. National Bureau of Standards high-alloy steel samples.

Results are summarized in Table I and a detailed survey of NBS steel 167 is given in Table II.

Acknowledgements—Thanks are due to the Louvain and Amsterdam cyclotron groups for irradiation facilities given, and to Dr. W. C. Orr, who corrected the English of the manuscript.

Zusammenfassung—Er wird eine Isotopenverdünnungsmethode ausgearbeitet zur Bestimmung von Vanadin in hochlegierten Stahlen. Das Vanadin wirt amperometrisch titriert nach Verflüchtigung vom Chrom als Chromyl-chloride. Die Vanadin Verluste durch Adsorption sind radiometrisch korrigiert worden.

Die Methode, geprüft an einer Anzahl NBS Stahlen, erwies sich als genau und reproduzierbar.

Résumé—On a mis au point une méthode de dosage du vanadium dans les aciers hautement alliés. La méthode est basée sur une titration ampérométrique, le chrome étant éliminé comme CrO_2Cl_2. Une correction radiométrique pour les pertes de vanadium dues à l'adsorption a été introduite au moyen de ^{48}V. Les résultats obtenus avec des aciers du NBS démontrent que la méthode est précise et reproductible.

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Talanta, 1958, Vol. 1, pp. 374–376. Pergamon Press Ltd., London.

A SPECTROPHOTOMETRIC METHOD OF DETERMINING SULPHURIC ACID CONCENTRATION*

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(*Received* 28 *July* 1958)

Summary—A spectrophotometric method of determining the per cent sulphuric acid in the concentration range 85 to 99% sulphuric acid was developed. It provides a rapid easy way of determining the concentration of sulphuric acid to within about ±0·3%. Quinalizarin is used as the colour-forming reagent.

A SPECTROPHOTOMETRIC method of determining the per cent sulphuric acid in the concentration range from 85 to 99% sulphuric acid has been developed. It involves the use of 1:2:5:8-tetrahydroxyanthraquinone (quinalizarin) as the reagent. The absorption spectra of quinalizarin dissolved in various concentrations of sulphuric acid shows absorbance maxima at 537 mμ, 575 mμ and 605 mμ and an isosbestic point at 585 mμ. The addition of water to the system increases the absorbance at 537 mμ and 575 mμ and decreases it at 605 mμ (Fig. 1).

The relationship between the ratios of absorbance at certain chosen wavelengths and the concentration of sulphuric acid has been studied to determine the best wavelengths to use.

EXPERIMENTAL

The exact concentration of quinalizarin used was not important since the ratio of the absorbances at two wavelengths is a constant for varying concentrations of coloured materials. Enough quinalizarin was used to ensure that the absorbance was within the measurable range on the spectrophotometer. Measurements of absorbance were made using a Beckman model B spectrophotometer. Ratios of the absorbances at the following pairs of wavelengths were determined and plotted versus per cent sulphuric acid: 535 mμ and 600 mμ, 535 mμ and 630 mμ, 575 mμ and 600 mμ.

The ratio of the absorbances at 535 mμ and 630 mμ gives the graph with the most favourable slope. A smooth curve is obtained from 85 to 99% sulphuric acid. The ratio reaches a minimum between 99 and 99·5% sulphuric acid and then increases sharply as the concentration of sulphuric acid is increased.

The ratios of absorbances were determined from three sets of experimental values for each acid concentration used. The acid concentration of each sample was determined by the titration of aliquot samples with standard sodium hydroxide. All of the experimentally determined points fell on the curve within ±0·3% of the acid concentration (Fig. 2).

This method provides a rapid, easy way of determining the concentration of sulphuric acid to within about ±0·3% sulphuric acid in the concentration range, 85 to 99% by weight.

Procedure

After a calibration curve has been determined, the only manipulations required are:

1. Dissolve a small amount of quinalizarin in about 3–5 ml of the acid. (The exact amount need not be known.)

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* Abstracted from a thesis submitted by Elaine Zimmerman in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1958.

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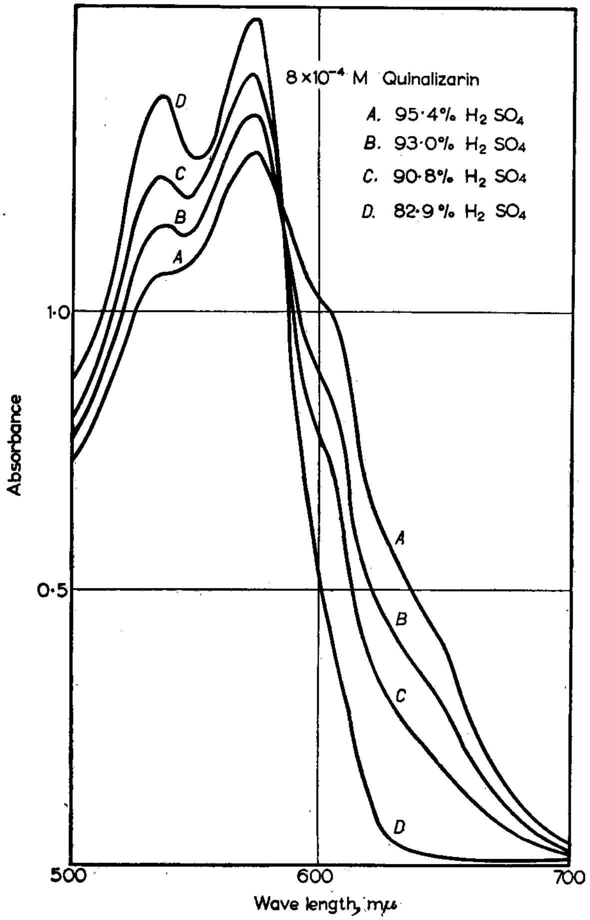

FIG. 1. Absorption spectra of quinalizarin in H_2SO_4.

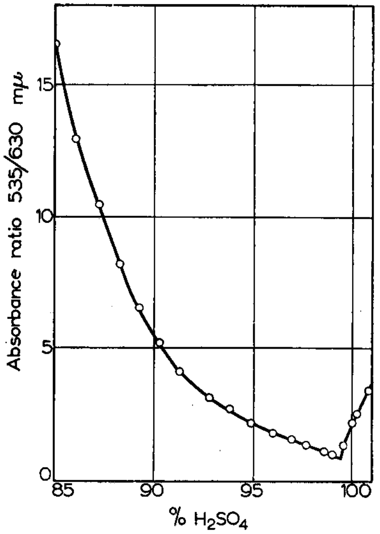

FIG. 2. Relationship between H_2SO_4 concentration and the relative absorbances of quinalizarin solutions at 535 mμ and 630 mμ.

2. Measure the absorbance of the solution at 535 mμ and at 630 mμ.
3. Calculate the ratio of the absorbances and read the percentage of sulphuric acid in the sample from the graph.

If coloured material is present in the sulphuric acid, the absorbances at 535 mμ and 630 mμ must be measured both before and after the quinalizarin is added. The ratio of the increase in absorbance at the two wave lengths is used to determine the percentage of sulphuric acid.

The presence of boric acid or borates in the sulphuric acid solution interferes. When borates are present the value for sulphuric acid concentration determined by this method is too high.

Acknowledgements—The authors wish to express their appreciation for the financial support given this project by the Standard Oil Research Foundation.

Zusammenfassung—Es wird eine spektralfotometrische Methode zur Bestimmung des procentigen Schwefelsäure-Gehalts in der Konzentrations-Reihe von 85 bis 99% von Schwelfelsäure entwickelt. Sie liefert ein rasches und einfaches Verfahren zur Bestimmung der Schwefelsäure-Konzentration bis innerhalb ungefähr ±0·5%. Man gebraucht Chinalizarin als das farbenbildende Reagens.

Résumé—Les auteurs ont mis au point une méthode spectrophotométrique qui permet de déterminer la teneur en acide sulfurique lorsque la concentration en acide sulfurique est comprise entre 85 et 99%. Cette méthode permet de déterminer d'une façon rapide et facile la concentration en acide sulfurique avec une précision voisine de ±0,3%. Le réactif qu'on utilise pour former la coloration est la quinalizarine.

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ARGENTOMETRISCHE TITRATIONEN MIT REDOXINDICATION

BESTIMMUNG VON HALOGENIDEN, CYANIDEN, RHODANIDEN UND KALIUM IN GEGENWART VON VARIAMINBLAU

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(*Received* 20 *March* 1958)

Zusammenfassung—Bei der argentometrischen Bestimmung von Halogeniden, Rhodaniden, Cyaniden und Kalium kann Variaminblau als Redoxindicator vorteilhaft angewendet werden. Durch Einstellung eines geeigneten pH–Wertes zeigt es den ersten Tropfen des Silbernitratüberschusses an. Potentiometrische Messungen mit einer Platinelektrode bezeugen die potentialbestimmende Rolle des Indicators am Anfang der Titration. Das Verfahren ist auch zur Silberbestimmung mit Kaliumjodidmasslösung geeignet. Kalium bestimmt man massanalytisch durch argentometrische Titration des Tetraphenylborats in Gegenwart des Redoxindicators.

Das System Ag–Ag$^+$ verhält sich infolge seines hohen Redoxnormalpotentials (+0,80 Volt) gegenüber Redoxindicatoren des Types Variaminblau als Oxydationsmittel. Wir berichteten schon darüber wie man diesen Umstand bei der ascorbinometrischen Silbertitration verwerten kann.[1]

Das Variaminblau[2] (4-Amino-4'-methoxy-diphenylamin HCl) umwandelt im pH-Gebiet 2–6 auf Einwirkung von milden oder geringen Mengen Oxydationsmitteln zu einem chinhydronartigen stark blauen Oxydationsprodukt (III), das teilweise zu Semichinonen (IV) dissociiert. In stärker oxydierenden Lösungen umsetzt das Chinhydron (III) zu einem Chinonimin (II). In stark sauren Lösungen (pH < 2) zersetzt sich das Chinonimin (II) rasch irreversibiler Weise infolge Hydrolyse zu Chinon-mono-4-methoxyanil (V), das keine Redoxindicatoreigenschaften mehr besitzt. Über pH 6 verschwindet infolge der freien Basenbildung (VI) die Chinhydronstruktur und die Lösung wird gelb (Abb. 1).

Das Umschlagspotential des Variaminblaus ändert im pH-Gebiet 2–6 laut Gleichung

$$E_i = +0{,}712 - 0{,}058\ \text{pH}$$

Durch Änderung des pH-Wertes der Lösung kann man also den Umschlagspunkt des Indicators innerhalb 364–596 mV beliebig einstellen. Das Umschlagsintervallum des Indicators erbreitet sich über ein Redoxpotentialgebiet von ±29 mV (Abb. 2.). Bei der Ermittelung dieser Daten beobachteten wir, dass die Redoxpotentiale des Systems Variaminblau Ox/Red, ähnlich dem System Chinon-Hydrochinon, sich sofort auf sehr gut definierte Werte einstellen. Diese Tatsache weist darauf, dass das System reversibel ist und sich als ein sehr guter Mediator verhält. Setzt man aus einer frisch bereiteten farblosen Indicatorlösung einige Tropfen zu einer Pufferlösung von gegebenem pH-Wert, so kann man in der Lösung mit Hilfe einer Platinelektrode sofort gut definierte Redoxpotentialwerte messen. Die reduzierte Form und die auf Einwirkung des Luftsauerstoffes sich bildende geringe Menge der oxydierten Form stellen sogleich einen Redoxpotentialwert ein, der in der noch farblosen Lösung mit 55–60 mV weniger als das Umschlagspotential beträgt.

Das Prinzip der Redoxindication über welche die vorliegende Mitteilung berichten wünscht, wird eingehender am Beispiel der argentometrischen Chloridbestimmung dargelegt.

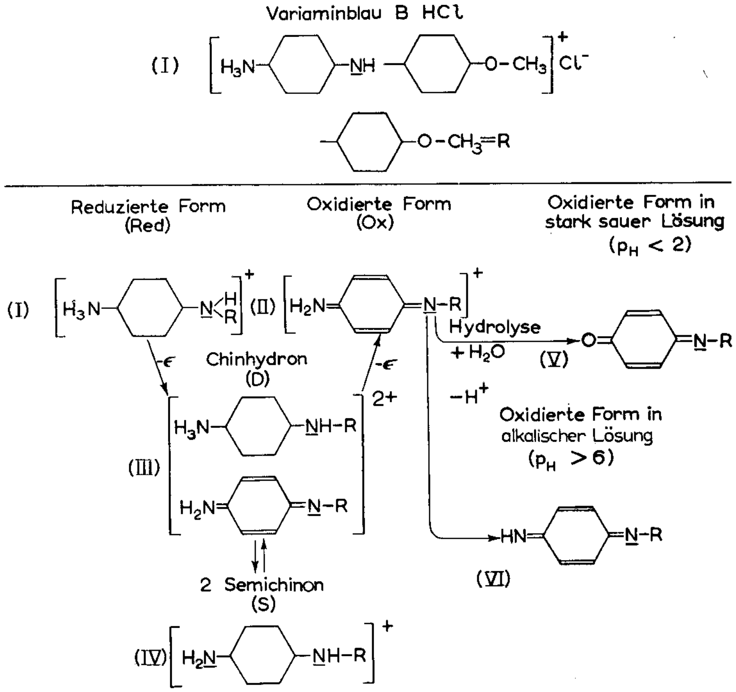

Abbildung 1. Redoxmechanismus des Indicators Variaminblau B.

Wird eine chloridhaltige Lösung mit einer Silbernitratmasslösung titriert, so nimmt die Silberionenaktivität $[\mathrm{Ag}^+]$ der Lösung in der Nähe des Äquivalenzpunktes sprunghaft zu, demzufolge wird das Redoxpotential der Lösung im Endpunkte der Titration ebenfalls positiver. Der Redoxpotentialwert stimmt in Gegenwart von Silbermetallspuren mit dem Elektrodenpotential des Silbers überein. Man kann diesen Wert aus folgender Gleichung berechnen:

$$E = +0{,}800 + 0{,}058 \log [\mathrm{Ag}^+]; \qquad \text{(bei } 20^\circ\text{)}$$

In neutraler und saurer Lösung ist der Elektrodenpotentialwert vom pH unabhängig. In Anwesenheit eines Chloridüberschusses berechnet man die Silberionenaktivität mit Hilfe des Löslichkeitsproduktes des Silberchlorids:

$$L = [\mathrm{Ag}^+] \cdot [\mathrm{Cl}^-] = 1{,}56 \cdot 10^{-10} \qquad \text{(bei } 20^\circ\text{)}$$

Das Redoxpotential des Äquivalenzpunktes berechnet aus dem Löslichkeitsprodukt des Silberchlorids beträgt

$$E_{\text{Äp}} = +0{,}800 + 0{,}058 \log \sqrt{L} = 0{,}520 \text{ Volt}$$

In Abb. 3 ist die potentiometrische Titrationskurve von 10 ml 0,1, 0,01 und 0,001 n Natriumchloridlösung zu sehen, d.h. die aus obigen Daten berechnete Abhängigkeit der. Redoxpotentiale von dem Grad der Titration (τ). Führte man die potentiometrische Titrationen in Gegenwart einer Silberindikatorelektrode aus, so erhielt man genau die theoretischen Werte.

Benützt man jedoch statt einer Silberelektrode eine Platinelektrode, so sind die Potentialwerte positiver als in Abb. 3 und auch unsicherer, im Äquivalenzpunkt aber erfolgt auch in diesem Falle ein deutlicher Potentialsprung (Abb. 3). E. Müller[3] erklärt diese Erscheinung damit, dass in der Lösung in sehr geringer Menge Argentoionen (Ag_2^+) anwesend sind. Das Redoxpotential der Lösung wird durch das System Ag^+—Ag_2^+ bestimmt.*

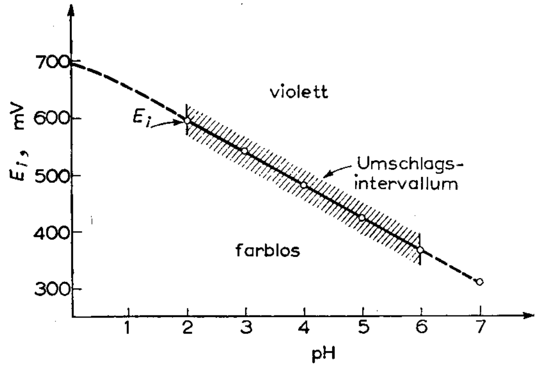

Abbildung 2. Änderung des Umschlagspotentials als Funktion des pH.

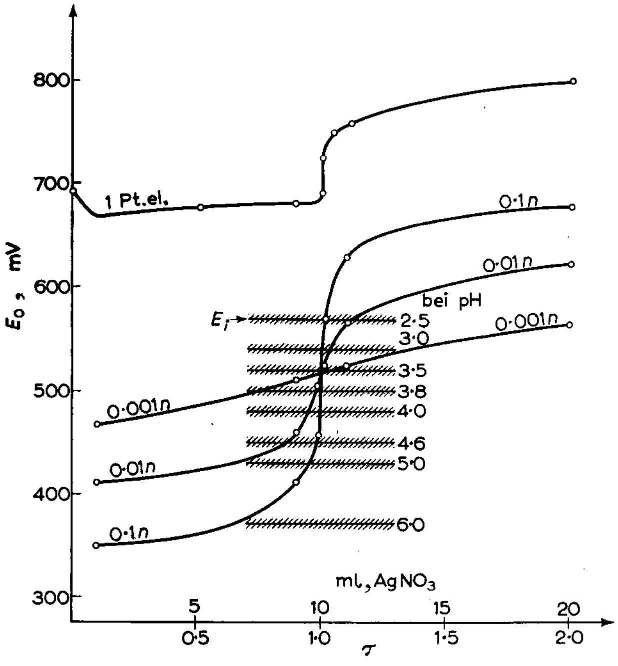

Abbildung 3. Potentiometrische Titrationskurve von Chloridionen.

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* Man gelangt zum mit Müller gleichen Resultat, wenn man annimmt, dass infolge der im Laufe der Messungen unvermeidlich eintretenden geringen Polarisation die Oberfläche der Platinelektrode mit wenig Silber legiert wird.

Den Potentialsprung des Endpunktes verursacht die sprunghafte Zunahme der Silberionenkonzentration. Besondere Verhältnisse entstehen dann, wenn die Titration in Gegenwart von Variaminblau in Anwesenheit einer Platinelektrode durchgeführt wird (Abb. 4). In diesem Falle bestimmt nämlich, solange die Chloridionen im Überschuss sind, das Variaminblau das Redoxpotential. Das als Indicator benützte reduzierte Variaminblau enthält nämlich immer eine bedeutende Menge (1—2%) der oxydierten Form. Dieses Redoxsystem übernimmt also in diesem Falle die Potentialbestimmung von dem in sehr geringer Konzentration anwesenden System Ag^+—Ag_2^+ Vor dem Äquivalenzpunkt hält also das Variaminblausystem ein von dem pH zwar abhängiges, aber während der Titration sehr beständiges Potential in der Lösung aufrecht. (Im Falle der Abb. 4 ungefähr 480 mV.) Diese Potentialwerte fallen immer unter das in Abb. 2 dargestellte Umschlagsgebiet. Nach dem Äquivalenzpunkt nimmt jedoch die Silberionenkonzentration sprunghaft zu, das Potential des Systems Ag^+—Ag_2^+ wird positiver als das des Systems Variaminblau Ox/Red, demzufolge wird das reduzierte Variaminblau oxydiert und es scheidet eine äquivalente Menge von metallischem Silber in Form eines feinen Pulvers aus:

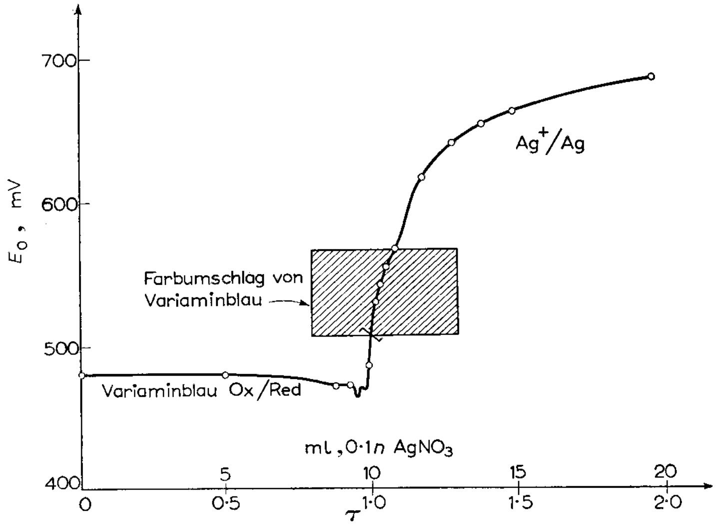

Abbildung 4. Potentiometrische Titrationskurve von Chloridionen in Anwesenheit von Variaminblau

$$\text{Variaminblau (Red)} + Ag^+ \rightleftharpoons \text{Variaminblau (Ox)} + Ag_{\text{Metall}}$$

Wird mit dem Silbernitratzusatz noch weiter verfahren, so bestimmt nun schon das System Ag^+—Ag das Potential, folglich stimmen die Potentiale mit den in Abb. 3 bei $\tau > 1$ messbaren Potentialen überein.

Chlorid

Abb. 3 enthält auch die Umschlagspotentialwerte des Variaminblaus bei verschiedenen pH-Werten. Das Umschlagspotential des Indicators ist bei pH-Wert 3,6 mit dem Potential des Äquivalenzpunktes (+520 mV) gleich. Aus den Titrationskurven ist es ersichtlich, dass man in 0,1 und 0,01 n Mass die Titration auch in essigsaurer Lösung (pH ∼ 3) ohne einen nennenswerten Indicatorfehler ausführen kann. In

0,001 n Mass ist es jedoch zweckmässig den pH-Wert mit einer Essigsäure-Natriumacetatpufferlösung vom pH 3,6 einzustellen. Potentiometrische Titrationen in Gegenwart des Indicators rechtfertigten diese Vorstellungen.

Wir gelangten im wesentlichen zu denselben Ergebnissen bei der Untersuchung der potentiometrischen Titrationskurven von Bromiden, Jodiden, Rhodaniden und Cyaniden. Führte man die Titrationen in Gegenwart einer Silberindicatorelektrode aus, so zeigten die Kurven einen mit dem Theoretischen übereinstimmenden Ablauf (Abb. 5, 6, 7). Im Falle der Anwendung einer Platinelektrode bestimmte vor dem Äquivalenzpunkt das System Variaminblau, danach das System Ag^+—Ag das Potential. Die Messungen zeigten, dass das Variaminblau vor dem Äquivalenzpunkt mit 55–60 mV niedrigere Potentiale gestaltet als das bei dem betreffenden pH-Wert beobachtbare Umschlagspotential; dies weist darauf, dass die Indicatorlösung 1–2% oxydiertes Variaminblau enthält, wenn auch die Lösung noch farblos ist. Nach dem Äquivalenzpunkt stimmen die Potentiale mit den unter Anwendung einer Silberelektrode gemessenen Potentialwerten. Abb. 5, 6, 7 enthalten auch die Umschlagspotentialwerte des Variaminblaus bei verschiedenen pH-Werten.

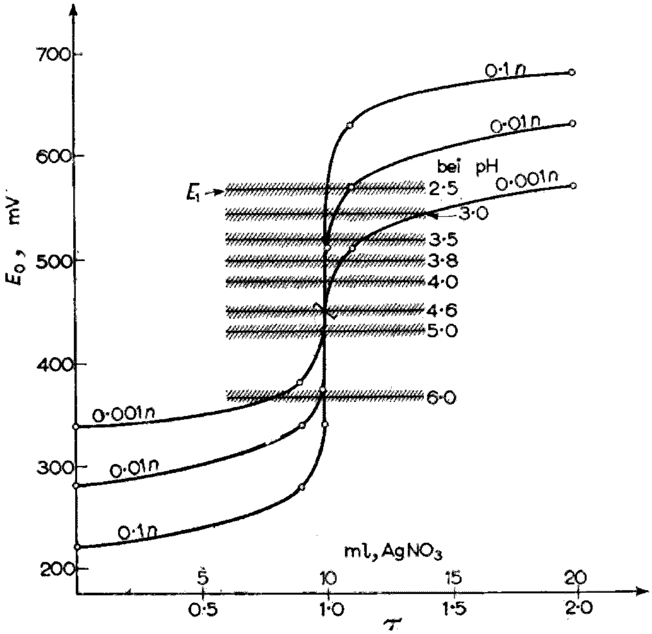

Abbildung 5. Potentiometrische Titrationkurve von Bromid- und Rhodanidionen.

Bromid und Rhodanid

Auf Grunde der Abb. 5 ist es leicht festzustellen, dass im Falle der Titration von Bromiden und Rhodaniden das Redoxpotential des Äquivalenzpunktes +460 mV beträgt, weiterhin, dass das Umschlagspotential des Variaminblaus in Lösungen vom pH-Wert 4,6 denselben Wert besitzt. Infolge der Steilheit der Titrationskurven zeigt jedoch der Indicator in Lösungen von über 0,01 n zwischen den pH-Werten 3–6, in 0,001 n Konzentration dagegen beim pH-Wert 4,5 mit befriedigender Genauigkeit (±0,2%) den Endpunkt an. Den geeigneten pH-Wert kann man also mit Essigsäure oder im Falle von sehr verdünnten Lösungen mit einer entsprechenden Pufferlösung einstellen.

Jodid

Die potentiometrischen Titrationskurven der argentometrischen Jodidbestimmung sind in Abb. 6 dargestellt. Das Äquivalenzpotential liegt in Anwesenheit einer Silberindicatorelektrode bei +330 mV. Das Variaminblau funktioniert bei pH-Werten über 6 nicht mehr gut als Redoxindicator, deshalb kann man sein Umschlagspotential nicht auf den Äquivalenzpunkt einstellen. Da jedoch in der Nähe des Äquivalenzpunktes die Titrationskurven sehr steil verlaufen, kann man den Indicatorfehler in Lösungen zwischen den pH-Werten 3,5–6 in 0,01 n und konzentrierterem Mass vernachlässigen. In 0,001 n Lösungenzeigt das Variaminblau zwischen den pH-Werten 4,6–6 genau den Endpunkt. In Gegenwart von Standardacetatpufferlösungen kann man folglich die Titration auch in sehr verdünnten Lösungen mit befriedigender Genauigkeit (±0,2%) beenden. In 0,1 n Mass genügt ein Ansäuern mit Essigsäure.

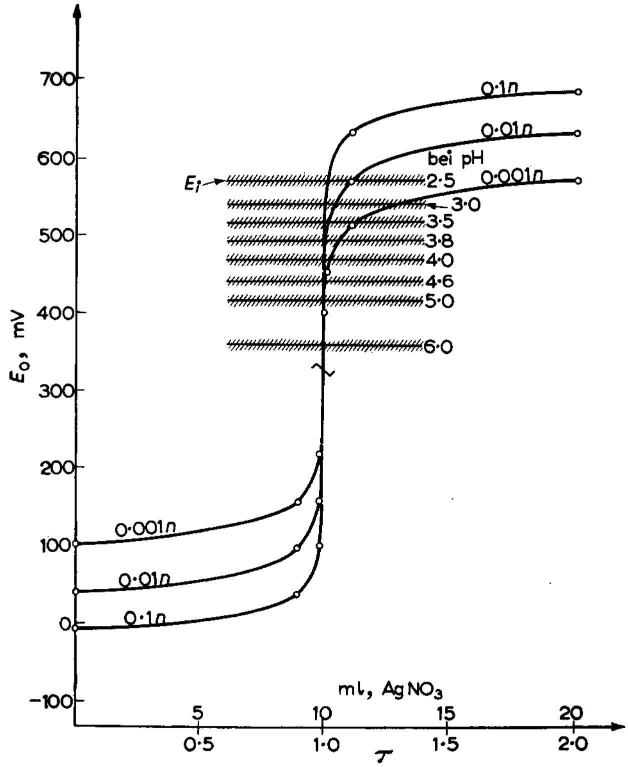

Abbildung 6. Potentiometrische Titrationskurve von Jodidionen.

Cyanid

Die neben Silberelektrode aufgenommene argentometrische Titrationskurve der Cyanide zeigt zwei scharfe Potentialsprünge (Abb. 7.) Der erste Potentialsprung kündigt den Endpunkt der Reaktion

$$2CN^- + Ag^+ = Ag(CN)_2^-$$

der zweite den von

$$Ag(CN)_2^- + Ag^+ = Ag[Ag(CN)_2]$$

an. Aus den Redoxpotentialwerten des Variaminblaus folgt, dass der Indicator nur zur Anzeige des zweiten Äquivalenzpunktes im Betracht kommen kann. Den Potentialwert dieses Punktes (+460 mV) nähert das Umschlagspotential des Variaminblaus am besten bei pH-Wert 4,3 an. Der Indicatorfehler ist aber praktisch auch noch in 0,001 n Lösungen vernachlässigbar, wenn der pH-Wert der Lösung zwischen 4–4,6 fällt. In Standardacetatpufferlösungen kann man also die Titration bei jeder praktisch in Betracht kommender Konzentration ausführen. In konzentrierteren Lösungen sind die Titrationskurven steiler, das pH-Intervallum ist folglich breiter. Im Falle der Titration von 0,01 n Cyanidlösungen kann der pH-Wert der Lösung zwischen den pH-Werten 3,5–5, im Falle von 0,1 n Cyanidlösungen zwischen 2,5–5 liegen. Dies bedeutet, dass in und über 0,01 n Mass zur Titration ein Ansäuern von Essigsäure genügt.

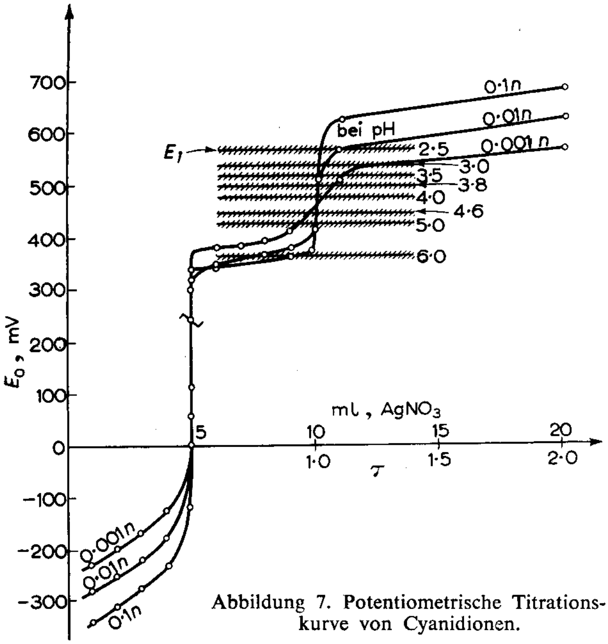

Abbildung 7. Potentiometrische Titrationskurve von Cyanidionen.

Die Variaminblauindication ermöglicht auch eine Cyanidbestimmung neben anderen Halogeniden. In diesem Falle titriert man die Cyanide nach Liebig bis zum Erscheinen der ersten beständigen Trübung, dann fügt man Variaminblau zur Lösung und titriert weiter bis dieses umschlägt. Subtrahiert man aus dem Gesamtmasslösungsverbrauch das Doppelte der nach Liebig verbrauchten Masslösungsmenge, so erhält man das den neben dem Cyanid anwesenden Haloiden äquivalente Volumen der Masslösung.

Titration von Silberionen

Die potentiometrische Titration einer Silberlösung neben einer Platinindicatorelektrode mit irgend einer Haloidenlösung zeigte, dass das Variaminblau im Äquivalenzpunkte nicht umschlug und dass das Redoxpotential der titrierten Lösung höher als das Umschlagspotential des Variaminblaus war. Nur im Falle einer Kaliumjodidmasslösung erfolgte ein Umschlag des Indicators und nur in diesem Falle gestaltete sich nach dem Äquivalenzpunkt das Redoxpotential der Lösung negativer als das Umschlagspotential des Variaminblaus. Diese Beobachtung wird folgendermassen erklärt: In einer silberhaltigen Lösung wird das Variaminblau sofort oxydiert und feinverteiltes Silber scheidet aus:

$$\text{Variaminblau (Red)} + Ag^+ \rightleftharpoons \text{Variaminblau (Ox)} + Ag_{\text{Metall}}$$

Titriert man nun die Lösung mit einer Chloridmasslösung, so reisst das sich bildende Silberchlorid das Silber mit sich, hüllt es ein, so dass letzteres das Variaminblau nun nicht mehr reduzieren kann. Das Silberhaloid erniedrigt also die Aktivität des metallischen Silbers in der Lösung, deshalb sich in der Lösung ein positiveres Redoxpotential nach dem Äquivalenzpunkt gestaltet, als es wäre falls die Silberaktivität nicht abgenommen hätte. Dies beweist auch ein Versuch, bei welchem zu einer titrierten Lösung feinverteiltes Silberpulver gestreut wurde. Auf Einwirkung des letzteren verschwand die Farbe des Variaminblaus und das Redoxpotential gestaltete sich negativer als das Umschlagspotential. Anders ist es im Falle von Kaliumjodid. Hier bestimmt nach dem Äquivalenzpunkt das System Jod-Jodid ($E_0 = +620$ mV) das Potential. Da der Kaliumjodidüberschuss Jod höchstens in Spuren enthalten kann, ist das Redoxpotential der überschüssiges Jodid enthaltenden Lösung negativer als das Umschlagspotential des Variaminblaus. Das Variaminblau wird folglich reduziert:

$$2\ \text{Variaminblau (Ox)} + 2J^- \rightleftharpoons 2\ \text{Variaminblau (Red)} + J_2$$

Bei den anderen Halogeniden kann so ein Redoxvorgang deshalb nicht stattfinden, weil die Normalpotentiale der Systeme Chlor-Chlorid bzw. Brom-Bromid wesentlich positiver sind.

Die Silberbestimmung mit Kaliumjodid führt man zweckmässig in fast neutralem Medium (pH = 4,6–6) aus und erwärmt im Endpunkte die Lösung auf 40–50 C° um den durch die Silberabsorption verursachten Fehler zu erniedrigen. In sehr verdünnter Lösung (>0,01 n) kann man jedoch diesen Fehler nicht mehr beseitigen, die Bestimmung ist also nur bis zu 0,01 n Mass ausführbar.

EXPERIMENTELLER TEIL

Lösungen

1% *ige Variaminblauacetat-Indicatorlösung*: Die technische Variaminblau B Base ist ein salzsaures Salz, dessen Chloridgehalt einen Fehler bei der argentometrischen Titration verursacht. Deshalb benützt man Variaminblauacetat, das auch beständiger als das Chlorid ist. Man bereitet es folgendermassen: Man wägt 0,2 g Variaminblau B Base in einen 100 ml Scheidetrichter, setzt 0,05–0,1 g Ascorbinsäure hinzu und löst das Gemisch unter kräftigem Umschütteln in 20 ml Wasser. Die Ascorbinsäure reduziert den ewentuell oxydierten Farbstoff. Dann fällt man mit 5 ml n Natriumhydroxydlösung die schlechtlösliche Variaminblau B Base, vermischt die niederschlaghaltige Lösung mit 20 ml Benzol, filtriert dann die benzolige Phase durch ein ebenfalls mit Benzol benetztes Filterpapier in einen zweiten Scheidetrichter. Die Extraktion wiederholt man nochmals mit 2–5 ml Benzol. Aus der gesammelten benzoligen Lösung bringt man das Variaminblau mit 20 ml 20% iger Essigsäure in die wässrige Phase zurück, die man dann durch ein benetztes Filterpapier in eine Tropfflasche filtriert. Aus dieser ungefähr 1% iger Indicatorlösung benützt man 3–6 Tropfen zu einer Titration. Die Indicatorlösung kann man 3 Wochen hindurch benützen. Man kann natürlich als Indicator auch das salzsaure Salz in 1% iger wässriger Lösung gebrauchen, man muss jedoch in diesem Fall den aus dem Chloridgehalt des Indicators sich ergebenden Fehler in Betracht nehmen. 1 ml 1% ige Variaminblau HCl–Lösung verbraucht 0,28 ml 0,1 n Silbernitratlösung.

Pufferlösung vom pH 3,6: 10,2 ml Eisessig und 2,8 g krist. Natriumacetat verdünnt man mit Wasser auf 1 Liter. 10 ml dieser Lösung fügt man zur neutralisierten, zu titrierenden Lösung.

Pufferlösung vom pH 4,6: Man löst 5,7 ml Eisessig und 13,6 g krist. Natriumacetat in Wasser und ergänzt auf 1 Liter. Aus dieser Lösung fügt man 10 ml zur neutralisierten, zu titrierenden Lösungen.

0,1 *n Essigsäurelösung*: Man verdünnt 6–7 ml Eisessig mit Wasser auf 1 Liter. Zur neutralisierten, zu titrierenden Lösungen fügt man davon 10 ml.

Alle diese Reagenzien und Lösungen prüft man mit Silbernitrat auf Chloridfreiheit.

Bestimmung von Chloridionen

Die 1–150 mg Chlorid enthaltende Lösung neutralisiert man mit chloridfreier Natriumhydroxydlösung oder Salpetersäure gegen Phenolphtalein bis die rosa Farbe eben erscheint, dann setzt man so viel 0,1 n Essigsäure hinzu, bis die Färbung wieder verschwindet. Nun versetzt man die Lösung mit 10 ml Pufferlösung vom pH 3,6 und 3 Tropfen Variaminblaulösung und titriert mit der entsprechenden Silbernitratmasslösung. In der Nähe des Endpunktes fügt man die Masslösung tropfenweise zu und schüttelt nach jedem Tropfen gründlich um. 1 ml 0,1 n Silbernitratmasslösung entspricht 3,5457 mg Chlorid.

Bemerkung: Beträgt die Konzentration der vorbereiteten neutralen Chloridlösung 0,01 n oder mehr, so kann man statt einer Pufferlösung mit 10 ml 0,1 n Essigsäure das pH einstellen.

Ergebnisse derartiger Titrationen sind in Tab. I dargestellt und wie ersichtlich sind sie sehr genau. Zur Ermittelung der Genauigkeit und der Standarddeviation des Verfahrens führten wir 12–12 parallele Titrationen aus, deren Ergebnisse in Tab. VII ersichtlich sind.

Aus den Daten sieht man, dass die Genauigkeit des Verfahrens die der Titration nach Mohr übertrifft. Ein weiterer Vorteil besteht in der Möglichkeit der Bestimmung in saurer Lösung. Diese Vorteile sind besonders bei der Bestimmung des Chloridgehaltes von natürlichen Wässern angenehm. Bei dem Mohr-schen Verfahren lässt der Farbumschlag des Chromatindicators viel zu wünschen, und es ergibt sich infolge des Indicatorfehlers ein bedeutender Masslösungsüberverbrauch.[4] Diese Fehler resultieren einerseits in der Streuung der Ergebnisse, anderseits dass mehr Chlorid gefunden wird als sollte. Den Indicatorfehler muss man deshalb hier immer in Korrektion nehmen.[4,5] Diese Korrektion beträgt laut Kolthoff in 150 ml Titrierendvolumen 0,6 ml 0,01 n Silbernitratlösung. Die Endpunktsindication mit Variaminblau ist viel besser wahrnehmbar, der Indicatorfehler (0,05 ml 0,01 n Silbernitratlösung in 100 ml Endvolumen) kann vernachlässigt werden. Tab. II enthält die Ergebnisse einiger Chloridbestimmungen von natürlichen Wässern mit Variaminblau und nach Mohr. Wie ersichtlich ist die Streuung der Variaminblautitrationen wesentlich geringer und die Ergebnisse liegen auch ohne Korrektion viel näher zum richtigen Wert als beim Mohr-schen Verfahren.

Bestimmung von Bromiden, Jodiden, Rhodaniden und Cyaniden

Die Lösung wählt man so, dass sie zwischen 0,4–400 mg Bromid, 0,6–600 mg Jodid, 0,3–300 mg Rhodanid, 0,1–140 mg Cyanid enthält. Diese Lösung neutralisiert man mit chloridfreier Natriumhydroxydlösung bzw. Salpetersäure bis Erscheinung der rosa Farbe des Phenolphtaleins, dann versetzt man sie mit soviel 0,1 n Essigsäure, dass die Färbung eben verschwindet, dann mit 10 ml Pufferlösung vom pH-Wert 4,65 und 3–6 Tropfen Variaminblauacetatlösung und titriert sie mit Silbernitratlösung. In der Nähe des Endpunktes fügt man die Masslösung tropfenweise zu und schüttelt nach jedem Tropfen kräftig um. 1 ml 0,1 n Silbernitratlösung entspricht 7,9916 mg Bromid, 12,691 mg Jodid, 5,9093 mg Rhodanwasserstoff bzw. 2,7027 mg Cyanwasserstoff.

Bemerkung: Bei oder über 0,01 n Halogenidkonzentration genügt zur pH-Einstellung 10 ml 0,1 n Essigsäure. Im Falle von Cyaniden wendet man zur pH–Einstellung in jeder Konzentration eine Pufferlösung von pH 4,65 an.

In Tab. III–VI sind die Ergebnisse von verschiedenen Halogenidbestimmungen dargestellt. In 12–12 parallelen Titrationen wurde die Standarddeviation und die Streuung der Ergebnisse bei 20 ml Masslösungsverbrauch ermittelt. (Tab. VII.) Wie daraus ersichtlich, liefert das Verfahren in 0,1 und 0,01 n Mass sehr genaue und auch noch in 0,001 n Mass befriedigende Ergebnisse.

TABELLE I.—TITRATION VON VERSCHIEDENEN MENGEN NATRIUMCHLORID MIT SILBERNITRAT IN ANWESENHEIT VON VARIAMINBLAUACETAT ALS INDICATOR

Einwaage 0,1 n, 0,01 n und 0,001 n NaCl-lsg. *ml*	In 0,1 n Lösungen			In 0,01 n Lösungen			In 0,001 n Lösungen		
	Verbrauch an $AgNO_3$-lsg. *ml*	Mittelwert *ml*	Abweichung %	Verbrauch an $AgNO_3$-lsg. *ml*	Mittelwert *ml*	Abweichung %	Verbrauch an $AgNO_3$-lsg. *ml*	Mittelwert *ml*	Abweichung %
5,05	5,07 5,04 5,05	5,05	±0,0	5,11 5,12 5,09	5,11	+1,20	5,05 4,99 5,00	5,01	−0,80
10,07	10,03 10,03 10,06	10,04	−0,33	10,12 10,11 10,14	10,12	+0,50	9,76 9,84 9,79	9,80	−2,70
20,02	20,02 20,04 20,03	20,03	+0,05	20,06 20,06 20,07	20,06	+0,20	19,95 19,87 19,92	19,91	−0,55
30,00	29,98 29,96 29,99	29,98	−0,07	29,97 30,04 30,00	30,00	±0,0	29,23 29,33 29,31	29,29	−2,40
49,96	49,86 49,83 49,83	49,84	−0,24	49,81 49,90 49,97	49,89	−0,14	48,26 48,21 48,27	48,25	−3,40

TABELLE II.—CHLORIDBESTIMMUNG IN TRINKWÄSSERN. TITRATION VON TRINKWÄSSERN (JE 100 ML) VERSCHIEDENER HERKUNFT MIT 0,01 n SILBERNITRATLÖSUNG IN ANWESENHEIT VON VARIAMINBLAUACETAT UND KALIUMCHROMAT ALS INDICATOREN

	In Anwesenheit von Variaminblauacetat (Korr. = — 0,05 ml)			In Anwesenheit von Kaliumchromat (Korr. = —0,40 ml)		
	Verbrauch an 0,01 n $AgNO_3$-lsg. *ml*	Mittelwert *ml*	Gefunden Cl^- *mg/Lit*	Verbrauch an 0,01 n $AgNO_3$-lsg. *ml*	Mittelwert *ml*	Gefunden Cl^- *mg/Lit*
Wasserleitungswasser unseres Laboratoriums	3,08 3,10 3,09	3,09 3,04*	11,0 10,8*	3,37 3,60 3,25	3,41 3,01*	12,1 10,7*
Wasserleitungswasser von Ujpest	2,84 2,81 2,81	2,82 2,77*	10,0 9,8*	2,95 3,41 3,19	3,18 2,78*	11,3 9,9*
Donauwasser von Vác	1,90 1,86 1,88	1,88 1,83*	6,7 6,5*	2,22 2,08 2,45	2,25 1,85*	8,0 6,6*
Wasserleitungswasser von Budafok	3,70 3,71 3,71	3,71 3,66	13,2 13,0*	3,86 4,14 4,06	4,02 3,62*	14,3 12,8*
Brunnenwasser von Budafok	4,81 4,77 4,80	4,79 4,74*	17,0 16,8*	5,13 5,01 5,34	5,16 4,76*	18,3 16,9*

* Die mit Sternchen bezeichneten Zahlen bedeuten die mit den Korrekturwerten verbesserten Ergebnisse.

TABELLE III.—TITRATION VON VERSCHIEDENEN KALIUMBROMIDLÖSUNGMENGEN MIT SILBERNITRATLÖSUNG IN ANWESENHEIT VON VARIAMINBLAUACETAT ALS INDICATOR

Einwaage 0,1 n 0,01 n und 0,001 n KBr–lsg. *ml*	In 0,1 n Lösungen			In 0,01 n Lösungen			In 0,001 n Lösungen		
	Verbrauch an $AgNO_3$–lsg. *ml*	Mittelwert *ml*	Abweichung %	Verbrauch an $AgNO_3$–lsg. *ml*	Mittelwert *ml*	Abweichung %	Verbrauch an $AgNO_3$–lsg. *ml*	Mittelwert *ml*	Abweichung %
5,05	5,07 5,06 5,06	5,06	+0,02	5,10 5,08 5,11	5,10	+1,00	5,34 5,30 5,39	5,34	+5,80
10,07	10,05 10,08 10,07	10,07	±0,0	10,11 10,14 10,13	10,13	+0,60	10,24 10,15 10,24	10,21	+1,40
20,01	20,01 20,00 20,01	20,01	±0,0	20,12 20,12 20,09	20,11	+0,50	20,19 20,30 20,28	20,26	+1,25
29,98	29,97 29,92 29,94	29,94	−0,11	30,05 30,03 30,06	30,05	+0,23	30,30 30,30 30,21	30,27	+0,97
49,93	49,75 49,73 49,75	49,74	−0,38	49,93 49,91 49,96	49,93	±0,0	50,09 50,12 49,98	50,06	+0,26

TABELLE IV.—TITRATION VON VERSCHIEDENEN KALIUMJODIDLÖSUNGSMENGEN MIT SILBERNITRATLÖSUNG IN ANWESENHEIT VON VARIAMINBLAUACETAT ALS INDICATOR.

Einwaage 0,1 n, 0,01 n u. 0,001 n KJ-lsg. *ml*	In 0,1 n Lösungen			In 0,01 n Lösungen			In 0,001 n Lösungen		
	Verbrauch an $AgNO_3$-lsg. *ml*	Mittelwert *ml*	Abweichung %	Verbrauch an $AgNO_3$-lsg. *ml*	Mittelwert *ml*	Abweichung %	Verbrauch an $AgNO_3$-lsg. *ml*	Mittelwert *ml*	Abweichung %
4,99	4,99 5,00 5,00	5,00	+0,20	4,99 5,00 5,00	5,00	+0,20	5,10 5,21 5,22	5,18	+3,8
9,91	9,92 9,93 9,94	9,93	+0,20	9,93 9,92 9,93	9,93	+0,20	10,12 10,11 10,02	10,08	+1,7
19,94	19,91 19,94 19,94	19,93	−0,05	19,98 19,97 19,96	19,97	+0,15	20,38 20,35 20,32	20,35	+2,05
29,91	29,88 29,91 29,90	29,89	+0,07	29,90 29,90 29,93	29,91	±0,0	30,52 30,48 30,40	30,47	+1,87
49,89	49,82 49,86 49,82	49,83	−0,12	49,90 49,87 49,90	49,89	±0,0	50,77 50,72 50,85	50,78	+1,78

TABELLE V.—TITRATION VON VERSCHIEDENEN KALIUMCYANIDLÖSUNGSMENGEN MIT SILBERNITRATLÖSUNG IN ANWESENHEIT VON VARIAMINBLAUACETAT ALS INDICATOR

Einwaage 0,1 n, 0,01 n u. 0,001 n KCN–lsg. *ml*	In 0,1 n Lösungen			In 0,01 n Lösungen			In 0,001 n Lösungen		
	Verbrauch an $AgNO_3$–lsg. *ml*	Mittelwert *ml*	Abweichung %	Verbrauch an $AgNO_3$–lsg. *ml*	Mittelwert *ml*	Abweichung %	Verbrauch an $AgNO_3$–lsg. *ml*	Mittelwert *ml*	Abweichung %
4,72	4,71 4,71 4,71	4,71	−0,21	4,58 4,54 4,59	4,57	−3,18	4,44 4,30 4,43	4,39	−6,99
9,43	9,41 9,42 9,40	9,41	−0,21	9,29 9,31 9,26	9,29	−1,49	9,21 9,13 9,23	9,19	−2,55
18,86	18,83 18,82 18,82	18,82	−0,21	18,63 18,58 18,70	18,64	−1,17	18,30 18,18 18,27	18,25	−3,23
28,29	28,19 28,20 28,20	28,20	−0,32	27,94 28,00 28,03	27,99	−1,06	27,70 27,88 27,87	27,82	−1,66
47,15	47,10 47,13 47,10	47,11	−0,08	46,79 46,72 46,83	46,78	−0,78	46,48 46,70 46,56	46,58	−1,21

TABELLE VI.—TITRATION VON VERSCHIEDENEN AMMONIUMRHODANIDLÖSUNGSMENGEN MIT SILBERNITRATLÖSUNG IN ANWESENHEIT VON VARIAMINBLAUACETAT ALS INDICATOR

Einwaage 0,1 n, 0,01 n u. 0,001 n NH_4SCN-lsg. *ml*	In 0,1 n Lösungen			In 0,01 n Lösungen			In 0,001 n Lösungen		
	Verbrauch an $AgNO_3$-lsg. *ml*	Mittelwert *ml*	Abweichung %	Verbrauch an $AgNO_3$-lsg. *ml*	Mittelwert *ml*	Abweichung %	Verbrauch an $AgNO_3$-lsg. *ml*	Mittelwert *ml*	Abweichung %
5,04	5,05 5,04 5,04	5,04	±0,0	5,06 5,02 5,04	5,04	±0,0	5,08 5,20 5,13	5,14	+2,00
10,05	10,09 10,09 10,10	10,09	+0,40	10,05 10,08 10,08	10,07	+0,20	10,18 10,04 10,14	10,12	+0,70
19,96	19,97 19,94 19,94	19,95	−0,05	20,11 20,07 20,10	20,09	+0,65	20,12 20,25 20,17	20,18	+1,10
29,94	30,01 29,98 29,98	29,99	+0,17	30,10 30,08 30,12	30,10	+0,53	30,38 30,37 30,30	30,35	+1,37
49,86	49,93 49,91 49,92	49,92	+0,12	50,12 50,05 50,07	50,08	+0,44	50,52 50,47 50,39	50,46	+1,20

TABELLE VII.—GENAUIGKEIT DER METHODE

Bestimmte Ionen	Konzentration n	Abweichung vom Sollwert %	Standarddeviation %
Cl^-	0,1 0,01 0,001	±0,0 +0,30 +0,50	±0,05 ±0,08 ±0,25
Br^-	0,1 0,01 0,001	±0,0 +0,40 +0,65	±0,06 ±0,10 ±0,19
J^-	0,1 0,01 0,001	±0,0 +0,15 +0,54	±0,04 ±0,08 ±0,16
CN^-	0,1 0,01 0,001	−0,32 −1,17 −3,22	±0,05 ±0,12 ±0,25
SCN^-	0,1 0,01 0,001	−0,10 +0,24 −0,96	±0,07 ±0,13 ±0,23
Ag^+	0,1 0,01	±0,0 +1,98	±0,06 ±0,51

Bestimmung des Jod- und Jodidgehaltes von Jodtinktur

Eine besondere praktische Bedeutung hat die Anwendung des neuen Verfahrens zur Wirkungswertbestimmung von Jodtinkturlösungen. Das neue Verfahren kann nämlich hier gut mit unserer ascorbinometrischen Jodtitration[6] verknüpft werden.

Verfahren: 2 ml der Jodtinktur pipettiert man in einen Titrierkolben, verdünnt sie mit 10 ml 50% igem Alkohol, titriert das Jod mit 0,1 n Ascorbinsäurelösung bis hellgelber Farbe, dann fügt man zur Lösung 20 ml Pufferlösung vom pH-Wert 4,65 und 3 Tropfen Variaminblaulösung und titriert bis Verschwinden der violetten Farbe. Aus dem Verbrauch berechnet man den freien Jodgehalt der Lösung. 1 ml 0,1 n Ascorbinsäurelösung entspricht 12,691 mg Jod.

Die mit Ascorbinsäure bis Farblosigkeit titrierte Lösung titriert man mit 0,1 n Silbernitratlösung weiter, bis die violette Farbe erscheint. Aus diesem Masslösungsverbrauch subtrahiert man das Volumen der aufs Jod verbrauchten Ascorbinsäurelösung. Die Differenz entspricht dem Kaliumjodidgehalt der Tinktur. 1 ml 0,1 n Silbernitratlösung entspricht 12,691 mg Jodid.

Bemerkung. Statt Ascorbinsäure kann man auch eine Natriumthiosulfatmasslösung neben Variaminblauindication benützen. Unsere Ergebnisse verglichen wir mit den Resultaten des Verfahrens nach der Vorschrift des ung. Arzneibuches VI; das zur Jodbestimmung eine Natriumthiosulfatmasslösung, zur Jodidbestimmung eine Silbernitratmasslösung und p-Äthoxychrisoidin als Indicator benützt. Die Ergebnisse stimmen ausgezeichnet überein. Unser Verfahren besitzt jedoch den Vorteil, dass es nur einen einzigen Indicator benötigt, dessen Umschlag sehr scharf ist (Tab. VIII).

TABELLE VIII.—JOD- UND KALIUMJODIDGEHALTBESTIMMUNG IN JODTINKTUR

1. Mit dem Verfahren des Ungarischen Arzneibuches

Einwaage Jodtinktur *ml*	Verbrauch an 0,1 n $Na_2S_2O_3$-lsg *ml*	Gefunden Jod *mg*	Mittelwert *mg*	Verbrauch an 0,1 n $AgNO_3$-lsg *ml*	Gefunden KJ *mg*	Mittelwert *mg*
2,00	8,57	108,7	108,6	11,29	45,2	45,3
	8,55	108,5		11,26	45,0	
	8,55	108,5		11,30	45,7	

2. Endpunktindication mit Variaminblau

Einwaage Jodtinktur *ml*	Verbrauch an 0,1 n Ascorbinsäure *ml*	Gefunden Jod *mg*	Mittelwert *mg*	Verbrauch an 0,1 n $AgNO_3$-lsg. *ml*	Gefunden KJ *mg*	Mittelwert *mg*
2,00	8,56	108,6	108,5	11,26	45,0	44,9
	8,55	108,5		11,26	45,0	
	8,54	108,4		11,25	44,8	

Silberbestimmung mit Kaliumjodidmasslösung

Die 5–550 mg Silberionen enthaltende Lösung neutralisiert man wie schon beschrieben, säuert dann mit einigen Tropfen 0,1 n Essigsäure an, versetzt mit 1–3 Tropfen Indicatorlösung und titriert mit 0,1 bzw. 0,01 n Kaliumjodidmasslösung. In der Nähe des Endpunktes erwärmt man auf 40–50 C° und titriert weiter bis Entfärbung der Lösung. 1 ml 0,1 n Kaliumjodidmasslösung entspricht 10,788 mg Silber.

Bemerkung: In Tab. IX. sind die Ergebnisse einiger Silbertitrationen dargestellt. Wie ersichtlich liefern die Bestimmungen bei verschiedenen Silberkonzentrationen gute Resultate. Die aus 12–12 parallelen Titrationen bestimmten Genauigkeits- und Deviationsdaten sind für den Fall der Bestimmung von 20 ml 0,1 n und 0,01 n Lösungen in Tab. VII zusammengefasst. Daraus geht hervor, dass in 0,1 n Mass sehr gute, in 0,01 n Mass noch annehmbare Resultate erzielt wurden.

Bestimmung von Kalium

Wir fanden, dass die Variaminblauindication auch zur argentometrischen Bestimmung der Tetraphenylborationen geeignet ist. Dieses Verfahren wurde zur volumetrischen Bestimmung der Kaliumionen erweitert. Wie bekannt, gibt das Natriumtetraphenylborat (Kalignost) mit Kaliumionen einen in Wasser sehr schlechtlöslichen Niederschlag,[7] der jedoch in Aceton löslich ist. Das Silbersalz des Tetraphenylborats, $Ag[B(C_6H_5)_4]$, ist jedoch sowohl in Wasser als auch in Aceton unlöslich. Das Tetraphenylboratanion kann man gleich den Halogeniden argentometrisch bestimmen:

$$[B(C_6H_5)_4]^- + Ag^+ = Ag[B(C_6H_5)_4]$$

Den Endpunkt dieser Titration kann man mit Variaminblauacetat auch in acetoniger Lösung ausgezeichnet indizieren. Der Vorteil dieser Indication gegenüber denen mit Adsorptionsindicatoren[8] bzw. Chromat[9] besteht darin, dass man sie unmittelbar ausführen kann und dass der Indicatorfehler und die Standardstreuung wesentlich geringer als bei den erwähnten anderen Verfahren sind.

Lösungen: 0,1 m *Natriumtetraphenylborat-(Kalignost)-lösung*: 3,42 g Natriumtetraphenylborat löst man in 100 ml Wasser. Zwecks Beseitigung einer ewentuellen Trübung klärt man die Lösung

TABELLE IX.—TITRATION VON VERSCHIEDENEN SILBERNITRATLÖSUNGSMENGEN MIT KALIUMJODIDLÖSUNG IN ANWESENHEIT VON VARIAMINBLAUACETAT ALS INDICATOR

Einwaage 0,1 n, 0,01 n $AgNO_3$ *ml*	In 0,1 n Lösungen			In 0,01 n Lösungen		
	Verbrauch an KJ *ml*	Mittelwert *ml*	Abweichung %	Verbrauch an KJ *ml*	Mittelwert *ml*	Abweichung %
4,95	4,92 4,94 4,92	4,93	−0,40	5,06 5,25 5,17	5,16	+4,2
9,86	9,84 9,83 9,84	9,84	−0,20	10,26 10,31 10,13	10,23	+3,8
19,64	19,63 19,66 19,63	19,64	±0,0	19,91 20,16 20,06	20,04	+2,0
29,43	29,34 29,35 29,33	29,34	−0,31	30,12 30,39 30,25	30,25	+2,8
49,01	48,88 48,90 48,90	48,89	−0,25	49,77 50,56 50,24	50,19	+2,4

durch 5 minutiges Schütteln mit 0,5 g Aluminiumhydroxyd oder Aluminiumoxyd und filtriert. 1 ml der Lösung ist zur Fällung von 3,5 mg Kalium geeignet. Es ist zweckmässig die Lösung stets frisch zu bereiten.

Waschflüssigkeit: 0,1 g des nach obiger Vorschrift gefällten und mit Wasser ausgewaschenen Kaliumtetraphenylboratniederschlages wird mit 250 ml Wasser während 30 Minuten geschüttelt, zur trüben Lösung dann 0,5–1 g Aluminiumhydroxyd oder Aluminiumoxyd gesetzt, einige Minuten hindurch umrührt, filtriert und die ersten 20 ml des Filtrats neuerdings auf das Filterpapier gegossen. Die Waschflüssigkeit muss vollständig klar sein.

Verfahren: Die 10–100 mg Kalium enthaltende Lösung verdünnt man auf 100 ml, säuert mit n Essigsäure gegen Lakmus eben an, dann setzt man zur Lösung in ungefähr 1,5-fachen Überschuss tropfenweise die 0,1 n Natriumtetraphenylboratlösung zu, filtriert in 5 Minuten durch ein dichtes Filterpapier und wäscht dann den Niederschlag mit der Waschflüssigkeit solange bis das Filtrat mit Silbernitrat schon kaum eine Reaktion zeigt. Das Filterpapier gibt man samt Niederschlag in das Glas, wo die Fällung erfolgte, zurück, giesst es mit 10–20 ml Aceton auf und löst den Niederschlag unter Umrühren mit einem Glasstab. Die acetonige Lösung säuert man mit 2 ml n Essigsäure an, fügt 3 Tropfen Variaminblaulösung hinzu und titriert mit der Silbernitratmasslösung bis zum Erscheinen der violetten Farbe. Gegen Ende der Titration titriert man tropfenweise und schüttelt nach jedem Tropfen kräftig um. 1 ml 0,1 n Silbernitratlösung entspricht 3,9096 mg Kalium.

TABELLE X.—MASSANALYTISCHE KALIUMBESTIMMUNG MIT HILFE VON KALIGNOST IN ANWESENHEIT VON VARIAMINBLAUACETAT ALS INDICATOR

Einwaage K+ *mg*	Gefunden K+ *mg*		Mittelwert *mg*	Abweichung %
11,75	11,75 11,71 11,71	11,66 11,69 11,66	11,70	−0,43
29,52	29,40 29,50 29,66	29,58 29,56 29,44	29,52	±0,0

Bemerkung: Ergebnisse von Kaliumbestimmungen sind in Tab. X ersichtlich. Wie es zu sehen ist, ist das Verfahren sehr genau.

Die Menge des zur Lösung gebrauchten Acetons kann die Genauigkeit der Bestimmung beeinflussen. Ein grosser Überschuss von Aceton löst nämlich eine nicht vernachlässigbare Menge des Silbertetraphenylboratniederschlages. Ist jedoch das Aceton zu wenig, dann scheidet in dem im Laufe der Titration sich allmählich verdünnenden Wasser–Acetongemisch auch das Kaliumtetraphenylborat aus. Beide Vorgänge verursachen einen negativen Fehler. Man wählt deshalb zweckmässig ein solches Acetonvolumen, dass es das zur Titration benötigte Masslösungsvolumen nicht übertrifft. Im allgemeinen sind im Falle der Bestimmung von Mengen unter 25 mg des Kaliums 10 ml Aceton genügend.

Benützt man zur Fällung eine Natriumtetraphenylboratlösung von bekanntem Volumen und Wirkungswert, so kann man auch derart verfahren, dass man die überschüssige Fällungslösung ohne Acetonzusatz rücktitriert. Dieses Verfahren liefert besonders im Falle von höheren Mengen Kaliums verlässliche Ergebnisse.

Summary—Variamine-blue can be used with advantage as a redox indicator in the argentometric determination of halide, thiocyanate, cyanide and potassium. At a suitable pH the first drop of silver nitrate in excess can be detected. The procedure may also be used for the determination of silver by means of potassium iodide. Potassium can be determined titrimetrically by argentometric titration of the tetraphenylboron compound in the presence of the indicator.

Résumé—On peut utiliser avec profit le bleu de variamine comme indicateur d'oxydo-réduction dans le dosage argentométrique des halogénures, du thiocyanate, du cyanure et du potassium. Il est possible de déceler, à un pH convenable, la première goutte de nitrate d'argent en excès. Le procédé permet également de déterminer l'argent au moyen de l'iodure de potassium. On peut effectuer le dosage titrimétrique du potassium par le titrage argentométrique du composé tétraphénylbore en présence de l'indicateur.

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THE QUANTITATIVE DETERMINATION OF FISSION AND NUCLEAR REACTION PRODUCTS

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Summary—Definitions are given to the terms "per cent atom burn-up" and "per cent atoms consumed" as applied to nuclear fuel analysis at the Argonne National Laboratory. The radiochemical and analytical methods which have been adapted and developed especially for this type of analysis are discussed. The analysis of nuclear reaction products by paper chromatographic methods and scintillation spectrometry is emphasised and demonstrated.

INTRODUCTION

INCREASED and more general operation of nuclear reactors for power will create a wider interest in the methods of determining the absolute numbers or the ratios of various nuclear events which have occurred in reactor fuels, blanket materials, moderators, and structural materials. The purpose of this paper is to summarise some of the calibrations and techniques employed, to indicate the type of instrumentation applicable, and to define and elucidate some special problems encountered in this type of analysis. The quantitative determination of radioactive nuclides in an extremely wide range of materials is becoming of increasing interest and importance. A relatively large part of the discussion is devoted to the methods which we have developed for determining the fraction of fissile atoms consumed by fission in nuclear fuels. This determination illustrates many of the basic methods of detection and calibration which are also applicable to the analysis of many other nuclear reaction products.

Although the counting methods are generally applicable, the particular decay scheme of each radioactive isotope must be considered when applying the various absolute counting techniques. This point is illustrated with the decay scheme of the fission product caesium-137, which has been useful in monitoring the number of fission events or per cent atom burn-up in nuclear fuels.

DEPLETION OF FUEL IN A NUCLEAR REACTOR

In the development of power reactors, nuclear fission is the most significant reaction. The fraction of fissile atoms which have undergone fission is an important quantity in analysing reactor performance. The number of other nuclear events which have occurred during the same time is compared to the total fission events to obtain the over-all neutron economy. Also, the total number of fission events which have occurred in a given fuel element is correlated with many other physical or chemical phenomena, such as dimensional changes, corrosion, phase changes, and other effects which take place during irradiation. Certain ambiguous terminology which has not been defined previously has developed in describing the total number of various events which occur in reactor fuel. This is especially true of the term "burn-up." The following definitions are suggested as generally applicable, and will be used here:

$$\text{Per cent total atom burn-up} = \frac{f_T}{(M_1{}^0 + M_2{}^0 + \ldots)\ 6{\cdot}02(10^{23})}\ 100 \qquad (1)$$

$$\text{Per cent total atoms consumed} = \frac{(f_T + C_M + \ldots)}{(M_1{}^0 + M_2{}^0 + \ldots)\ 6{\cdot}02(10^{23})}\ 100 \qquad (2)$$

where $(M_1{}^0 + M_2{}^0 + \ldots)\ 6{\cdot}02(10^{23})$ is the number of atoms of a definite element or group of elements in the original sample. It is generally more convenient, and at higher per cent total atom burn-up necessary, to obtain the denominator by an analysis before irradiation. Mass analysis may also be applied, and the molar and isotopic content of the sample used to group only the fissile isotopes in the denominator of (1) and (2) to give the per cent fissile atom burn-up and the per cent fissile atoms consumed.

f_T is the total number of fissions detected in the original group of atoms, $(M_1{}^0 + M_2{}^0 + \ldots)\ 6{\cdot}02\ (100^{23})$. There is no reliable method to distinguish between fission of the various fissile isotopes. Therefore the selection of the original group of atoms in a complex fuel should include all the fissile atoms and non-fissile atoms which will breed fissile atoms, and result in an appreciable contribution to the value of f_T. Two of the more important examples are:

$$^{232}\text{Th} \xrightarrow{(n,\gamma)} {}^{233}\text{Th} \xrightarrow[23\ \text{min}]{\beta^-} {}^{233}\text{Pa} \xrightarrow[27\ \text{d}]{\beta^-} {}^{233}\text{U}$$

$$^{238}\text{U} \xrightarrow{(n,\gamma)} {}^{239}\text{U} \xrightarrow[23\ \text{min}]{\beta^-} {}^{239}\text{Np} \xrightarrow[2{\cdot}3\ \text{d}]{\beta^-} {}^{239}\text{Pu}$$

C_M is the total number of relatively stable non-fissile atoms in an irradiated sample which are formed by neutron capture with a fissile isotope in the selected group of atoms. These atoms may or may not have been converted to other elements by radioactive decay. It should be apparent that the term C_M cannot be defined exactly unless referred to a specific fuel composition, and even then fissile, non-fissile and nuclear stability of the non-fissile atoms are applied within the judgements of the analyst. The important point is that as burn-up values and the complexity of fuel compositions increase, the application of the term C_M must be made with reference to the system being analysed.

Other nuclear reactions with the selected group of atoms may be included in a similar manner. The per cent total atom burn-up and per cent total atoms consumed are referred to the original atom content of the sample. The analysis of the atom content, however, may only be made on a sample after the irradiation. If there is a significant burn-up and isotopic change, the elemental and isotopic content as observed on the irradiated sample should be corrected, where appropriate, to the original atom content.

Thus, the atom content of the denominators of (1) and (2) may be expressed by

$$(M_1{}^0 + M_2{}^0 + \ldots)6{\cdot}02(10^{23}) = M_1 + M_2 + \ldots)6{\cdot}02(10^{23}) + f_T + C_M{}^1 + \ldots \qquad (3)$$

where $(M_1 + M_2 + \ldots)6{\cdot}02(10^{23})$ is the atom content of the irradiated sample.

$C_M{}^1$ is the number of atoms which were formed by capture from atoms in the group $(M_1{}^0 + M_2{}^0 + \ldots)6{\cdot}02(10^{23})$, but would not be analysed as a part of the group $(M_1 + M_2 + \ldots)(6{\cdot}02)(10^{23})$ in the irradiated material.

In general, the addition of the number of atoms fissioned is sufficient to correct the analysis of the irradiated material to the original content. In many cases the neutron capture products are relatively stable and the chemical analysis will not be changed. However, if the atoms comprising the denominators of (1) and (2) are selected by both the isotopic and elemental content, the correction of the irradiated sample analysis would be applicable.

With high burn-up values, it is not possible to deduce the original fuel content accurately by analysis of the irradiated material alone. Therefore, the values of per cent total atom burn-up and per cent total fissile atoms consumed must be obtained on a confined sample whose elemental and isotopic content has been analysed before the irradiation. Other considerations which must be taken into account when analysing an unconfined sample are the state of the material, the temperature, and proper sampling. Finely divided material or a very thin sample will allow a substantial fraction of the fission fragments to recoil from the sample, and gaseous fission products will diffuse out at appreciable rates. The fission product content of the sample is then no indication of the number of fission events which have occurred in the sample. Molten uranium or plutonium will lose additional gaseous and volatile fission products. Caesium is distilled from uranium and plutonium at their melting points. Fused salts and solutions may be more troublesome because of surface deposition of fission products and loss of gaseous fission products if the sample is not confined during irradiation. Thick fuel elements will attenuate the neutron flux in the element. Consequently, fission and other nuclear reaction products will not be generated homogeneously throughout the fuel. Because of the difficulties outlined above, it is very often impossible to obtain a representative sample on unconfined reactor fuel. The sampling problems associated with attenuation of the neutron flux will, of course, affect any method of analysis.

The fission reaction requires a careful absolute fission yield calibration before any fission product may be used to determine the number of fission events which have occurred in a given material. This calibration will be discussed in the experimental section to follow. Other than fission, the only nuclear reaction which will deplete significant amounts of fissile material in a reactor is the neutron capture reaction. Other reactions, such as $(n, 2n)$, (n, α), (n, p), etc., will be of interest if the products formed have very high neutron cross sections, by virtue of the radiation effects of the products, or for theoretical reasons.

DETERMINATION OF FISSION BY FISSION PRODUCT MONITORING

The direct measurement of fission events in a sample has relatively limited practical application. Direct measuring includes counting individual fission events with a proportional ionisation counter[8,13] and measuring the total heat released by fission. Indirect methods are fission product monitoring and observation of changes in the isotopic ratio of fissile and non-fissile isotopes of a heavy element.

The measurement of total heat released is generally applied to a complete pile assembly rather than individual isolated samples. Monitoring a heavy sample by means of a light sample plus a fission counter is the most sensitive method,[8] but this has severe practical limitations. This method has been applied[13] to calibrate the indirect fission product procedure for the determination of per cent total atom burn-up in uranium-235 and plutonium-239.

Of the indirect methods, fission product monitoring is the most sensitive indicator of the number of fissions which have occurred. Isotopic analysis has advantages in that the sample is not subject to errors due to the recoil, volatilisation, or surface adsorption of fission products from an unconfined sample. The isotopic composition of the fuel, however, is affected by nuclear reactions other than fission. The ratio of σ_c/σ_f for uranium-235, for example, varies[14] with position in a typical fast reactor from 0·14 to 0·27. Also, resonance capture cross sections may be very high and give abnormal isotopic compositions at certain pile locations. In general, the sensitivity of the isotopic ratio analysis is not high enough for samples irradiated to relatively low (10^{-4} to 10^{-1} per cent) burn-up.

Only a few of the fission products are suitable for determining the number of fission events. The useful fission products are limited to the mass numbers falling on, or close to, the heavy or light fission yield peaks. Fission products located on the sharp slopes or in the valley of the fission yield curve show relatively large variations in their fissions yields with changes in neutron energy or the fissile isotope. Even on the heavy or light fission yield peaks, appreciable variations in the yield with neutron energy and fissile isotopes make accurate calibrations laborious. It is also desirable to be able to analyse a relatively wide variety of pile-irradiated samples with irradiation histories involving one to two years. In order to avoid detailed, tedious half-life corrections, it is necessary to select a long-lived fission product. The analytical chemistry of the fission product selected should be straight forward, and the counting characteristics favorable, to allow a reliable sample isolation and accurate count. Caesium-137 meets the above requirements.

The calibration of caesium-137 and absolute fission yields in fast pile flux for uranium-235 and plutonium-239 have been reported.[13] Thermal fission yields of caesium-137 for various fissile isotopes have been reported.[19] In reviewing the recent literature on some absolute fission yields and the half-life of caesium-137, one finds a discouraging lack of agreement. Thermal fission yield of caesium-137 for plutonium-239 has been reported[19] as 5·8 and also[21] as 4·94 per cent. The half-life of caesium-137 is also subjected to uncertainty. Values reported recently are $32{\cdot}6 \pm 2$ years,[20] $30{\cdot}9 \pm {}^{0\cdot3}_{0\cdot4}$ years,[3] and $26{\cdot}6 \pm 0{\cdot}4$ years.[22] Although precision of $\pm 1{\cdot}5$ per cent may be obtained be careful fission product analysis and counting techniques, our uncertain knowledge of the absolute fission yields and decay constants limits the accuracy of monitoring fission events by a fission product. Strontium-90, the only other long-lived peak-yield fission product which we have considered acceptable, is subject to essentially the same limitations in accuracy as caesium-137.

The use of $^{140}\text{Ba} \rightarrow {}^{140}\text{La}$ is not suitable except for very short irradiations. Fuel samples are usually in the pile for months or years, and the ^{140}Ba content would indicate only the most recent irradiation history of the sample.

It is possible to prepare a heavy foil of fissile material with a known number of fission events. This has been done[13] in a fast pile flux bath for uranium-235 and plutonium-239. The fission product isolated from such foils at known chemical yield may then be used to calibrate a stable counting system. This circumvents the limitations in accuracy caused by the uncertainties in absolute fission yield and decay constants. However, this is not generally applicable to all fissile materials with the required accuracy and without relatively formidable experimental difficulties. In the long run, more accurate decay constant and absolute fission yield data will be useful in improving the accuracy and general applicability of the fission product method for monitoring the number of fission events.

To complete the fission product monitoring method for the number of fission events which have occurred in a nuclear fuel sample, two additional aspects must be considered—the counting method and the chemical isolation of the fission product. Caesium-137 has been used as the monitor for fission events for the past seven years by the authors, and has been described briefly in a previous paper.[4] Caesium-137 counting was first done on calibrated, long-lived, halogen-filled Geiger counters. At present, samples of low irradiation levels are counted with a methane flow end-window proportional counter. The caesium-137 samples, with appreciable caesium-134 or caesium-136 content, are counted with calibrated sodium iodide–thallium-activated scintillation crystals. When fission foils[13] of a particular fissile element are not available, the basic calibration is made with a 4π-methane flow counter and the reported caesium-137 yield values. The techniques used in preparing 10 microgram/cm^2 resin sample films and the detector design, etc. are those described by B. D. Pate and L. Yaffe.[15–18]

The decay scheme of caesium-137 is relatively well known. The checks we have obtained between the 4π-counter and independently calibrated scintillation spectrometers are better than five per cent. The absolute calibration of scintillation crystals has been discussed by P. R. Bell.[2] In the 4π-counter 110·5 counts are recorded for every 100 caesium-137 atoms disintegrating. One hundred of these counts come directly from beta rays emitted during caesium decay, while 9·7 come from subsequent conversion electrons. These delayed conversion electrons originate from the isomeric state of barium-137, which is formed in 92 per cent of the caesium-137 decays. In 10·6 per cent of the decays of the barium-137 isomer, conversion electrons are emitted. Approximately one per cent of the remaining unconverted 661 keV gamma rays is counted in the methane flow counter. This will add an additional 0·8 count for every 100 caesium atoms disintegrating for the total 110·5 counts.

The most important contribution of the scintillation spectrometer in burn-up analysis is in correcting the caesium count for presence of caesium-134 or caesium-136. Figure 1 shows the changes in the gamma spectrum of isolated caesium from natural uranium at various per cent total uranium atom burn-up. In these samples, the caesium-136 yield was initially low and approximately sixty days cooling was required to reduce the caesium-136 activity level below detection. The method employed in making the caesium-134 correction may vary with the instrument available. A scintillation spectrometer with reasonably good resolution will almost completely resolve the caesium-134 795 keV and the caesium-137 661 keV gamma rays. By integrating from the valley between these two gamma rays, a counting rate will be obtained which is proportional to the caesium-134 content alone. Since pure caesium-134 is also easily prepared by pile irradiation of caesium-133, the proper proportionality constant can be obtained by counting pure caesium-134 under the same conditions as the mixed caesium-137, -134 isotopes. With a magnetic core multichannel analyser, the combined spectrum of caesium-137, -134 is inverted in the memory of the instrument. A pure caesium-134 sample is then counted at the same geometry until the 795 keV line is just subtracted out when the spectrum is viewed on the oscilloscope display.

Figures 2 and 3 show the gamma scintillation spectrometer response curves of pure caesium-134 and caesium-136. The caesium-136 was prepared from uranium-233 fission. The yield of the shielded nuclide caesium-136 is relatively high (0·12 per cent) for uranium-233 fission, and green caesium isolated from a short irradiation of uranium-233 has only a small caesium-137 activity level, as shown in Figure 3. The yield of caesium-136 for plutonium-239 fission is approximately 0·09 per cent, and for uranium-235 fission the yield is 0.006 per cent. Therefore, it should be noted that more cooling time is required for plutonium-239 and uranium-233 burn-up samples to reduce the caesium-136 level. The area under the full energy peak of caesium-137 can be obtained fairly accurately in the presence of some caesium-136, as the caesium-136 gamma spectrum does not contain an unresolved gamma ray in the 661 keV region.

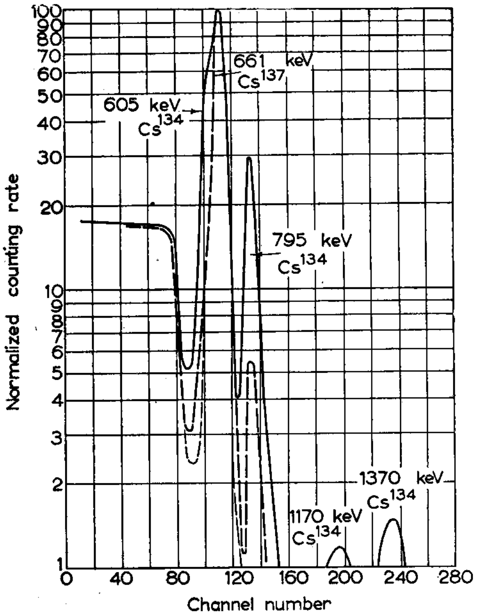


FIG. 1.—Changes in the gamma spectrum of caesium with the per cent total natural uranium atom burn-up

——— 1·7 per cent total uranium atom burn-up

— — 0·33 per cent total uranium atom burn-up

– · · · 0·04 per cent total uranium atom burn-up

Several methods are suitable for the chemical isolation of caesium. The procedure of Glendenin and Nelson[9] has been satisfactory. The chemical yield was obtained by weighing the perchlorate on a glass fibre filter mat. The area and uniformity of the sample spread were controlled by slurrying the caesium perchlorate precipitate in a glass chimney placed over the filter mat. A procedure[7] for caesium extraction with sodium tetraphenylboron and nitrobenzene has also been used successfully. Recently, amyl acetate has been substituted[6] for the less desirable nitrobenzene solvent. The method for isolating caesium at present used in this laboratory for a majority of the

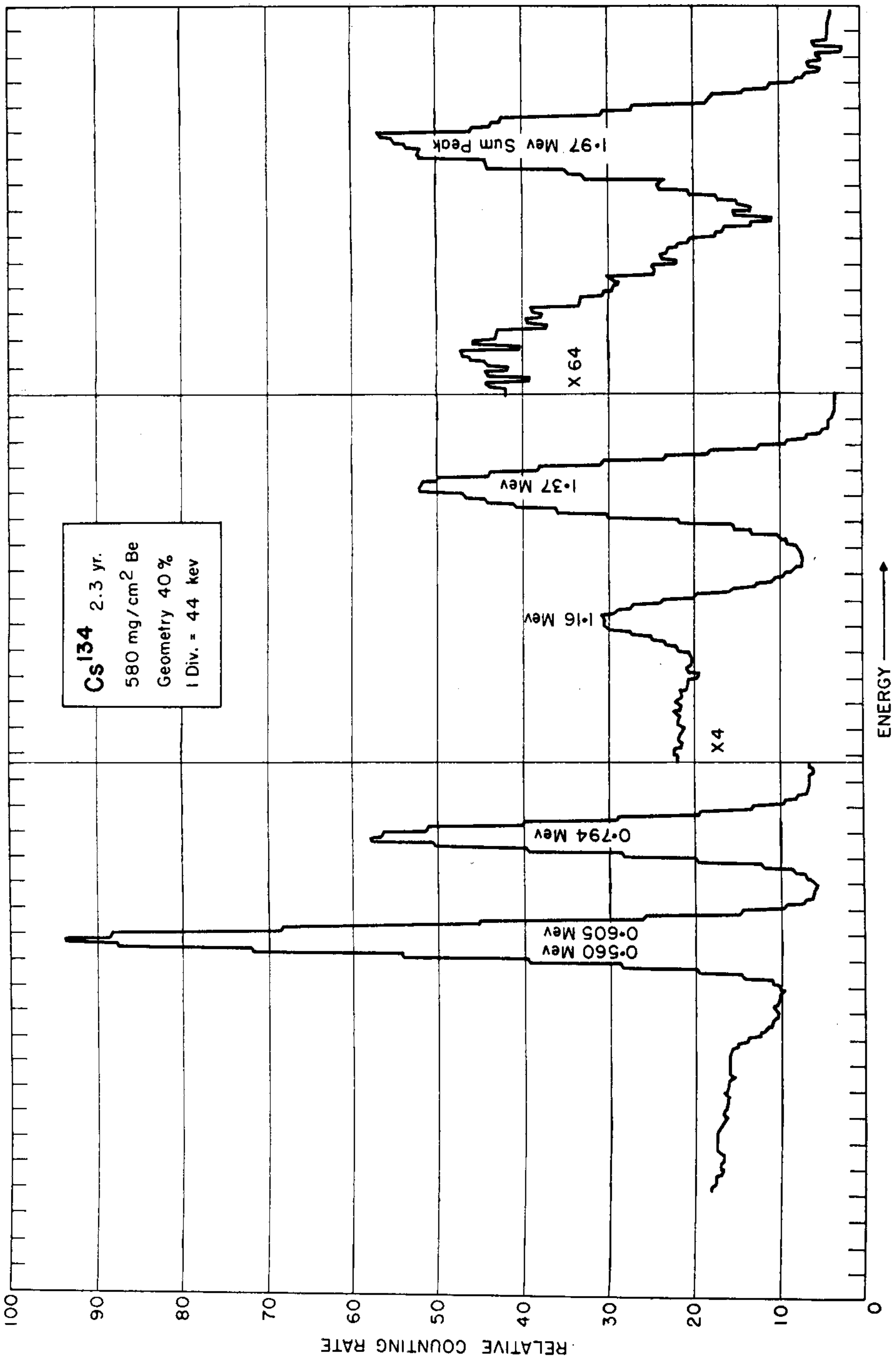

Cs^{134} 2.3 yr.
580 mg/cm^2 Be
Geometry 40%
1 Div. = 44 kev
0·560 Mev
0·605 Mev
0·794 Mev
1·16 Mev
1·37 Mev
1·97 Mev Sum Peak
X 4
X 64
ENERGY
RELATIVE COUNTING RATE
100
90
80
70
60
50
40
30
20
10
0

FIG. 2.

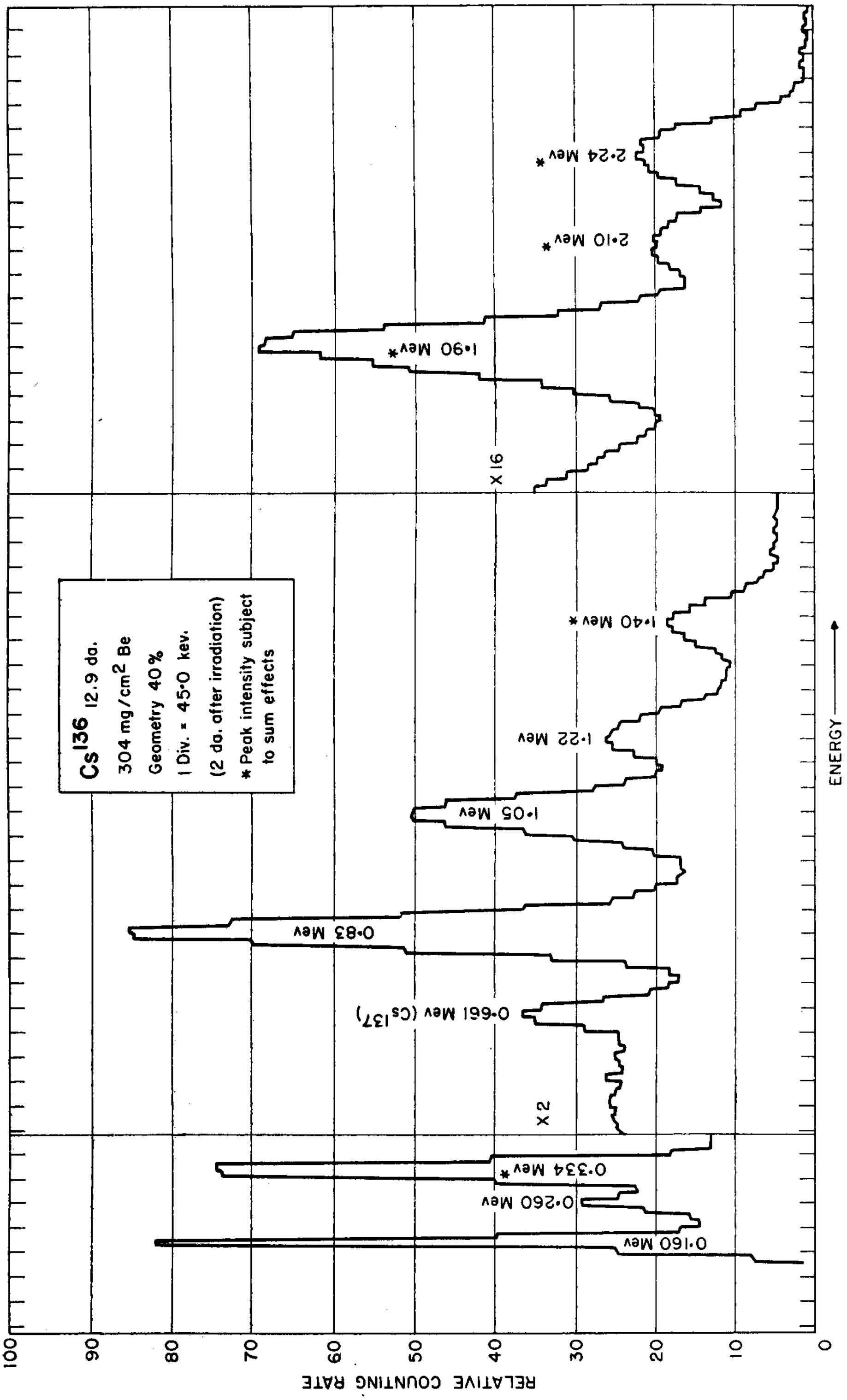

Cs^{136} 12.9 da.
304 mg/cm^2 Be
Geometry 40%
1 Div. = 45·0 kev.
(2 da. after irradiation)
* Peak intensity subject to sum effects
0·160 Mev
0·260 Mev
0·334 Mev*
X 2
0·661 Mev (Cs^{137})
0·83 Mev
1·05 Mev
1·22 Mev
1·40 Mev *
X 16
1·90 Mev*
2·10 Mev*
2·24 Mev*
0
10
20
30
40
50
60
70
80
90
100
RELATIVE COUNTING RATE
ENERGY

Fig. 3a.

burn-up samples is an ascending paper chromatographic analysis.[4] Samples of very low burn-up values which require analysis of a large amount of fissile fuel will still require one of the former procedures. Figure 4 shows radioautographs of a typical "fissium" fuel and a calibrated caesium-137 sample after chromatographic analysis. The yield of caesium by this analysis is 100 per cent. Sample solutions of nitric or hydrofluoric acids give somewhat better chromatograms than hydrochloric acid solutions. The fissile fuel solutions containing from 2–100 micrograms of uranium were placed in Whatman 3 MM paper and air dried. The developing solvent was a mixture of 60 g of 49 per cent hydrofluoric acid and 100 ml of dry methyl ethyl ketone. The chromatograms require 3 to 5 hours to develop. The caesium is easily located at the centre of the chromatogram with a simpler Geiger counter probe equipped with a defining slit over the window. The paper is cut and mounted between 25 mil mylar plastic and counted with a scintillation spectrometer. The absolute d/m is obtained by comparing the counting rates under the 661 keV gamma peak of the samples and $4\pi\beta$-calibrated caesium-137 solution chromatographed as shown in Figure 4.

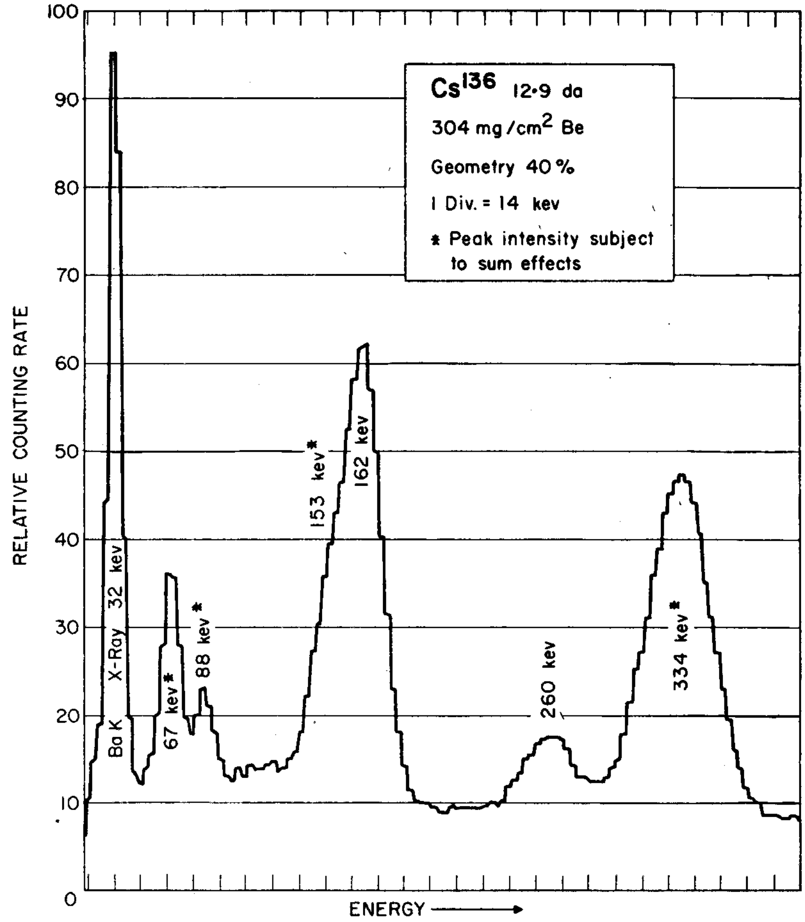
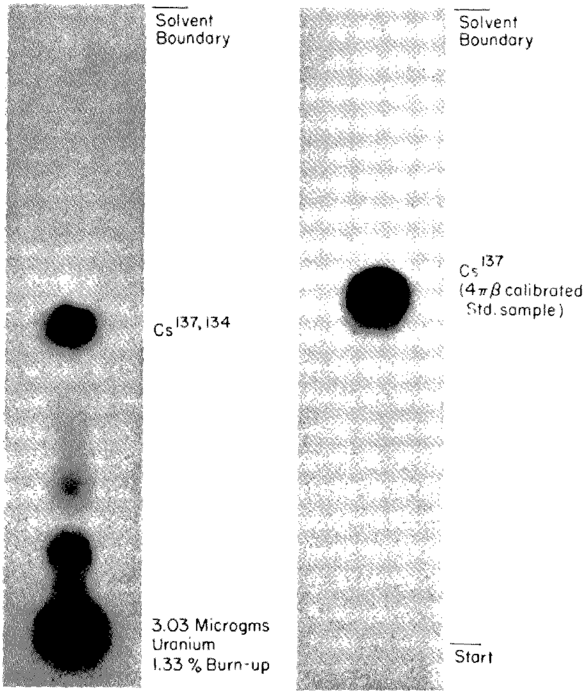


FIG. 3b.

FIGURE 4

CHROMATOGRAPHIC ANALYSIS OF CESIUM FOR PERCENT TOTAL URANIUM ATOM BURN-UP DETERMINATION

(FUEL COMPOSITION: U-95% WITH Mo, Ru, Pd, Rh, Zr AND Nb)



It has been observed that carrier-free caesium solutions show a marked tendency to adsorb on the walls of glass and plastic containers. Over 50 per cent of the carrier free caesium-137 in $2M$ hydrochloric or $2M$ nitric acid has been lost from solution in a month of storage. The addition of approximately one microgram of caesium carrier per ml has stabilised the $4\pi\beta$ calibrated solutions for a period of six months. The same amount of carrier is also added to burn-up samples during dissolution.

THE ASSAY OF NEUTRON CAPTURE AND OTHER NUCLEAR REACTION PRODUCTS

In many reactor problems, it is necessary to correlate the per cent atom burn-up with the formation of other nuclear reaction products. A typical example is the determination of the ratio of neutron capture events of a nuclide to fission events of a particular nuclide or a group of nuclides. The two most useful assay methods are radiochemical and mass spectrometric.

The methods of 4π-counting and scintillation counting are applied as discussed in the previous section for the assay of caesium-137. In each case, some knowledge of the particular decay scheme must be applied as in the case of caesium-137, which has been shown above in detail.

Many heavy element capture reactions produce unstable nuclei in which all the disintegrations go through an alpha branch. It is then possible to determine the absolute d/m to 0·5 per cent or better, with a low geometry alpha counter or a 2π-geometry alpha counter. The 2π-alpha counting will require thinner, more uniformly spread samples for an accurate assay. Jaffey[12] has given a comprehensive discussion of alpha assay instrumentation and methods. Samples which have been alpha-assayed may be used to calibrate a scintillation counter or beta counter. In many experiments, it is not possible or desirable to build up the specific activity of the capture nuclide high enough so that alpha pulse analysis or mass analysis may be applied.

Sodium iodide crystals have been standardised with alpha-assayed americium-241 samples. The intensity of the 59·6 keV gamma transition, as observed with a sodium–iodide scintillation crystal under controlled conditions, was correlated with the disintegration rate. Of the alpha transitions 36·4 per cent also involves the 59·6 keV gamma transition. Gamma assay is often preferred or necessary, rather than alpha or beta assay, because of the rigorous requirements of sample preparation for the latter. Nevertheless, the experimental conditions for calibration and scintillation counting must be carefully defined and maintained. For example, the counting rate of americium-241 under the 59·6 keV full energy peak varies, because of the escape of iodine X-rays from the sodium–iodide crystal. The fraction of X-radiation which escapes is a function of the counting geometry, being a maximum with nuclear radiation striking the crystal at the edges or with small angles of incidence with the crystal surface. Attenuation of the X-rays must be kept constant or negligible. The sample mount is also selected so that secondary scattering is not a factor in the assay.

Neptunium-239 disintegration rate has been accurately determined by $4\pi\beta$-counting. This nuclide, appearing after neutron capture by uranium-238, has an intense unresolved 106 keV gamma and a 104 keV X-ray from both Pu-239 *m* isomeric state and K-conversion. Sixty-five per cent of the disintegrations of neptunium-239 resulted in 104–106 keV photons in the energy range. ^{238}U mono-energetic neutron capture events with Van de Graaff irradiations have been monitored directly in natural uranium metal foils by the authors. A uranium foil of the same material as that irradiated is used to subtract the uranium daughter activity and background. R. C. Axtmann and J. S. Stutheit[1] have previously reported a similar method for monitoring pile-irradiated samples.

Protactinium-233, appearing after neutron capture of throium, contains relatively low energy beta radiation, which makes accurate $4\pi\beta$-counting difficult. Very pure neptunium-237, however, can be obtained and alpha-assayed absolutely. The known protactinium-233 daughter atom content in secular equilibrium with neptunium-237 can then be correlated with the gamma spectrum. The area under the group of unresolved 302–342 keV Pa-233 gamma rays has been used to calibrate scintillation crystals for the determination of protactinium-233 atom content, and thus the neutron capture events which have occurred in thorium targets.

The application of mass analysis for the determination of the number of atoms in irradiated material may require the accurate determination of abundance ratios of adjacent masses in the heavy elements to values as high as 10^5 to 10^6. It is important, therefore, to employ machines and techniques which are specially adapted to this type of analysis. A review of instruments and techniques to 1952 has been compiled by Inghram and Hayden.[10] Mass analysis of samples is obtained at present with a 60°, 12-inch radius mass spectrometer with a multiple filament ionization source. The multiple filament ionization source[11] allows the measurements to be obtained on metal ions rather than the oxide ions. The scattering background under these conditions at one mass unit from the high abundance peak of a heavy element is two parts per million. Accurate analyses of heavy element capture products have been made to 20 parts per million[14] of the adjacent high abundance peak.

Acknowledgement—The authors wish to thank Peter Kafalas, Milton Levenson, Ellis Steinberg, David Okrent, and Richard Vogel for many helpful discussions and criticisms. Also, they wish to acknowledge the assistance and co-operation of Willard McCorkle and Joseph McMillen in carrying out the pile experiments. Allen Madson and Gene McCloud have carried out experiments associated with the burn-up analyses.

Zusammenfassung—Die Definitionen der Ausdrücke "per cent atom burn-up" und "per cent atoms consumed" in ihrer Anwendung auf Kernbrennmaterial-Analyse in Argonne National Laboratorium werden angegeben. Die radiometrischen und analytischen Methoden, die für diesen Analyse-Typus besonders angepasst und entwickelt worden sind, werden erörtert. Die Analyse der Kern-reaktionprodukte durch papierchromatographische Methoden und Spektrometrie wird betont und gezeigt.

Résume—On donne les définitions des termes "per cent atom burn-up" et "per cent atoms consumed" dont on se sert dans l'analyse de combustible nucléaire dans le Laboratoire National d'Argonne. Les méthodes radiochimiques et analytiques qui ont été adaptées et mises au point exprès pour ce genre d'analyse sont discutées. On insiste particulièrement sur l'analyse des produits de réactions nucléaires par chromatographie sur papier et par spectrométrie à scintillation, et on décrit ces méthodes.

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PRELIMINARY COMMUNICATIONS

The determination of metals in organic compounds by the closed flask method

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THE closed oxygen flask method has become widely used in recent years for the determination of sulphur and halogens in organic compounds.[1] It has lately been applied in the determination of phosphorus[2,3] and, since the present work was started, it has been extended to the determination of mercury.[4] It seemed possible that this simple means of decomposition might be applicable as a general procedure for the determination of many metals in organic compounds, hence a selected range of metal-containing organic compounds has been examined. The method was quite successful with certain metals but with others some difficulties were encountered. Silicon-containing compounds were not examined for obvious reasons, nor were compounds containing metals which give difficultly soluble oxides after ignition, *e.g.* aluminium and iron, nevertheless an examination of such compounds might repay investigation. It should be emphasised that only a few compounds of each type were examined. Further work is undoubtedly necessary to establish the most favourable conditions for the decomposition, absorption and titration of all types of compound containing a particular metal; and the purpose of this paper is to indicate the possibilities of the general technique. In order to make the procedures as general as possible, EDTA was used for the titration wherever applicable.

Zinc, cadmium and magnesium

Compounds containing these metals could be burnt without difficulty and the combustion products were absorbed in *N* hydrochloric acid solution. When nitrogenous compounds were analysed, nitrogen oxides, which interfered with the indicator used in the EDTA titration, were decomposed by warming with sulphamic acid. Typical results are shown in Table 1.

TABLE I

Compound	% Metal	
	Found	Theor.
Zinc benzoate	21·77 ± 0·1	21·58
Zinc lactate	22·44 ± 0·2	22·37*
Zinc dibenzyl dithiocarbamate	10·72 ± 0·28	10·71
Magnesium oxinate	6·85 ± 0·35	6·90
Cadmium oxinate	28·55 ± 0·2	28·1
Trifluoromethylphenyldiethylphosphine-cadmiumdiiodide	19·28 ± 0·4	18·99
Di-(trifluoromethylphenyldiethylphosphine)-cadmium tetraiodide	10·11 ± 0·4	10·24
Potassium tetraphenylboron (B determined)	2·99 ± 0·08	3·02
Sodium tetraphenylboron (B determined)	3·16 ± 0·07	3·20

* Determined by a standard method

Procedure: Weigh the sample (5–10 mg) on to filter paper and ignite in the oxygen flask (250–ml) in the usual way.[1,3] The absorption solution is 5 ml of 1*N* hydrochloric acid. Shake the flask thoroughly and allow to stand for at least 20–30 minutes. After having rinsed the stopper and platinum gauze with water, neutralise the solution approximately with ammonia and add 10 ml of

0·005M EDTA, 5 ml of buffer solution (67·5 g of ammonium chloride and 570 ml of concentrated ammonia diluted to 1 litre with water) and 2 drops of 0·5% ethanolic Solochrome Black 6B indicator solution. Titrate the excess of EDTA with a 0·005M magnesium chloride solution to the first appearance of a red colour.

For nitrogen-containing compounds, after rinsing the gauze, suck the air from above the solution at the pump, add several crystals of sulphamic acid, bring just to the boil, cool, neutralise with ammonia, and proceed as above.

For iodine-containing compounds, remove the iodine from the solution by dropwise addition of 1% sodium bisulphite solution until a slight excess is present. Then add a slight excess of 10% formaldehyde solution before proceeding to the neutralisation.

In all determinations, blank tests were run.

Boron

Only two compounds containing boron were available and the amounts of boron present were small. The results were satisfactory at this level (Table 1) but compounds containing higher amounts of boron require testing. To avoid risk of contamination from the usual borosilicate flask, a soda-glass flask was used.

Procedure: Burn the sample in a soda-glass flask containing 10 ml of water as absorbent. Complete the determination by acidimetric titration in the presence of mannitol.[5]

Arsenic

Some attention was given to the method of completion. The quinoline[3,6] method and the bromate method were preferable to various iodometric finishes. During the decomposition of the sample some arsenic was lost by alloying with platinum; this was proved by spectrographic analysis of used wires. Other materials were substituted for platinum; with glass, nickel, nichrome or inconel spirals, either the combustion was unsatisfactory or contamination of the wire still occurred. Platinum has a definite catalytic effect on the combustion and is therefore to be preferred. The formation of an arsenic-platinum alloy is usually assumed to occur only in a reducing atmosphere and this may have been present at the platinum surface at the moment of ignition. However, when the filter paper used to enwrap the sample was impregnated with potassium nitrate, bromate, persulphate or perchlorate, the arsenic recoveries were still slightly low although the combustion took place under stronger oxidising conditions. Of the various reagents tested, potassium nitrate was by far the most satisfactory; the ignition proceeded vigorously but safely and nitrate-impregnated paper might be satisfactory for general use with refractory materials.

Surprisingly, with the standard compound used, arsanilic acid, most of the arsenic was in the tervalent state after the ignition, hence the bromate titration was preferred after the reduction of the small amount of arsenic^{V}. Eventually it was concluded that the flask method for the determination of arsenic has no advantage over the method of Schulek and Villecz[7] and no further attempt was made to solve the problem of the alloy formation.

Antimony compounds were not examined because of the probability of similar behaviour. Again the method of Schulek and Villecz would seem preferable to the flask method.

Other metals

Lead and bismuth compounds were tested with an absorption solution of 3 ml of concentrated nitric acid. Both metals alloyed with platinum, the alloy formation being particularly evident in the case of lead. Further work is required to overcome these effects. In some instances, the alloy could probably be dissolved off the wire and the platinum^{IV} masked with cyanide before the titration.

Certain metals, *e.g.* nickel and gallium, formed insoluble oxides which could not be dissolved by solvents convenient for the subsequent EDTA titration.

Conclusion

Of the metals examined, zinc, cadmium, magnesium and boron offered no unusual difficulties over the range of organic materials available. For arsenic and antimony, the method seemed less advantageous than those already available. Alkali and alkaline earth metals were not examined but it seems likely that flame photometry would be suitable for their determination after the combustion. A silica flask would probably be necessary because of contamination from ordinary glass. Further investigations will fall into three categories: (1) the extension of the method to other metals and to a wider range of compounds; (2) the establishment of the optimum conditions for absorption of the combustion products; and (3) the resolution of the problem of alloy formation with platinum which is serious in some cases. In the meantime it can be concluded that the flask method is a promising means of decomposing some organo-metallic compounds although it cannot at present be considered generally applicable.

Acknowledgment—We wish to express our sincere thanks to Miss Marie Marks for her assistance in carrying our some of these experiments.

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The adherence to Beer's law of solutions of ammonium chloro-iridate and similar compounds

(*Received* 9 *October* 1958)

In 1956, Spitzy, Magee and Wilson[1] confirmed the formation of quinquevalent rhenium by reduction of perrhenate in sulphuric acid solution with bismuth amalgam, and applied this to the determination of rhenium. During the course of recent work in this laboratory in which quinquevalent rhenium was obtained by the above method, it was found that on standing the blue rhenium^{V} solution was transformed into a deep purple solution, with sedimentation of a black powder. The assumption that this change was due to disproportioning of the rhenium^{V} into 4- and 6-valent forms, with deposition of ReO_2 is being investigated polarographically, and the results will be reported later.

It was also observed, in the preparation of potassium perrhenate solutions in sulphuric acid for reduction, that if the concentration of the sulphuric acid was greater than 34*N*, potassium perrhenate (Specpure) dissolved, not with formation of a colourless solution (as in less strongly acid solutions) but with the formation of a solution identical in colour with the disproportioning quinquevalent solutions. The absorption spectra of both solutions were identical.

It is supposed, therefore, that in the solutions in concentrated sulphuric acid the SO_2 impurity reduces a small amount of potassium perrhenate to the 5-valent state, and that this in turn disproportions to rhenium^{IV} and rhenium^{VI} as before.

At a recent extended discussion[2] concerning the existence of mixed valency states in the compound $(NH_4)_2IrCl_6$, it was stated[3] that the deep purple colour of that compound was evidence of the presence of mixed valencies. No-one present, however, was able to confirm that solutions of that compound obey Beer's law. As there appeared to be an obvious similarity between the ammonium chloro-iridate system and the rhenium system which we are investigating, it was considered useful to examine the adherence to Beer's Law of solutions of ammonium chloro-iridate and the rhenium system. Since it is not supposed that mixed valency states of ammonium chloro-osmate exist, this compound was also included for direct comparison with the other systems. This communication reports the results of this investigation.

Ammonium chloro-iridate

An aqueous solution containing 0·03 g/100 ml of this compound was prepared, and the absorption spectrum was examined. Absorption maxima were found to occur at 305 mμ, 416 mμ, 435 mμ and 490 mμ. Measurements were carried out in subsequent work at 305 mμ, 435 mμ and 490 mμ.

A series of accurate dilutions of the original solution of ammonium chloro-iridate were prepared, and the spectral densities of the solutions at the above wavelengths were determined. The plot of extinction against dilution factor produced a curve showing marked deviations from Beer's law.

The rhenium system

To compare this system with the ammonium chloro-iridate, a solution containing 0·082 g/100 ml of potassium perrhenate in $36N\ H_2SO_4$ was prepared. The absorption spectrum of this solution has a marked maximum occurring at 513 mμ. Measurements were made at this wavelength.

A series of accurate dilutions of the original solution were prepared, and the plot of extinction against dilution factor produced a curve showing deviation from Beer's law.

Ammonium chloro-osmate

An aqueous solution of this compound containing 0·004 g/100 ml was prepared, and it was found that absorption maxima occur at 309 mμ, 425 mμ and 480 mμ. A series of dilutions of the original solution were prepared. The plot of extinction against dilution factor, in contrast to the other two systems, showed complete adherence to Beer's law.

Conclusion

The results obtained in the above investigations lend support to the view that mixed valencies occur in the ammonium chloro-iridate and the rhenium systems. It will be of interest to extend these investigations to related compounds, and to examine the results obtained from a complete polarographic study, from which indisputable evidence should be obtained.

The investigations described above will be reported in detail subsequently.

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BOOK REVIEWS

Radioisotope Laboratory Techniques. R. A. FAIRES and B. H. PARKS. George Newnes Ltd., London, 1958. pp. xii + 244. 25s. net

THE rapid proliferation of radiochemical techniques has made it difficult for the specialist to keep abreast of new developments in the field. For the neophyte, the task is virtually impossible. Specialised instrumentation for these techniques has developed along with the techniques themselves, and an entire new industry has sprung up to manufacture and sell the equipment which is essential to the modern radiochemical laboratory.

In many laboratories, the use of radioisotopes for analytical purposes has become almost routine. Biochemists, in particular, have seized on radioactive tracers with enthusiasm, so that many analyses which were either impossible or prohibitively time-consuming are now performed rapidly and with precision by laboratory technicians. Inorganic analysts have been somewhat slower to adopt radiochemical methods, preferring instead to use the more "classical" methods of gravimetry, titrimetry and spectroscopy.

To some extent, this reluctance is traceable to an exaggerated fear of the hazards attendant on the handling of radioactive materials. A more valid reason, however, lies in the substantial capital investment required to outfit a radiochemical laboratory. The radiochemical analyst needs not only the standard analytical equipment—balances, centrifuges, glassware, furnaces, etc.—which must be kept separate from similar equipment for non-radioactive work, but he must also have electronic measuring and recording equipment which may rival a mass spectrometer in cost and complexity. In addition, the radiochemical analyst requires an isolated laboratory to guard against the spread of contamination. He must have special waste-disposal and personnel-monitoring facilities for control of radiation hazard. If the radiochemist is not himself well versed in electronic equipment maintenance, he must either have available the services of specialists or learn to do a substantial amount of maintenance and trouble-shooting himself.

The analytical chemist or laboratory director charged with the responsibility of initiating a radiochemistry programme is certainly entitled to sympathy, at the very least, if he has qualms as he approaches the task of justifying such a programme.

There are many excellent books which deal with the theory of radiochemistry and nuclear physics. Others discuss, in considerable detail, the various experimental applications of radiochemistry in analysis. There are relatively few comprehensive sources, however, which deal with the practical problems of setting up a radiochemical laboratory and putting it to use. The authors, in this book, have made a useful contribution to this problem. In twenty well-edited chapters, they have covered virtually the entire range of subject matter which should be of interest to the beginning radiochemist or to the general analytical chemist who wishes to broaden his professional background.

The first three chapters deal with elementary nuclear physics and radiochemical concepts, giving the reader sufficient background information for his intelligent use of the remainder of the book. Chapter titles include: Introduction to Health Physics; The Laboratory; Decontamination and the Disposal of Waste; Particle Detectors and Their Use; The Statistics of Counting; The Choice of Counting Equipment; and Some Chemical Applications. None of the chapters is definitive; one cannot, for example, read the four chapters on electronic techniques and equipment, and feel equipped to do battle with a 100-channel pulse-height analyser. On the other hand, the authors describe in detail exactly how to prepare a zinc sulphide screen for alpha scintillation counting and name specific sources of supply in Great Britain.

One of the more useful qualities of the book is the recognition by the authors that certain laboratory practices, which are peculiar to radiochemistry and not readily learned except through experience, have not been adequately described. Thus, for example, they devote several paragraphs to the important, though apparently trivial, matter of the proper procedure for putting on and removing a pair of rubber gloves.

The chapter on "Feasibility" will be of particular interest to those who are uncertain as to the possible usefulness of radiochemistry in the solution of their own problems. Several examples are given of feasibility calculations, including one which shows that it would be impractical to label golf balls with cobalt-60 in order to locate them with a Geiger counter.

Both of the authors are associated with the Isotope School at Harwell, and the pedagogical approach, devoid of pedantry, makes for a book of welcome clarity and considerable value.

H. W. KIRBY

Differential Thermal Analysis. W. J. SMOTHERS and Y. CHIANG. Chemical Publishing Co., New York, 1958. pp. 444. $16.00.

THIS book is a comprehensive review of the literature on differential thermal analysis (D.T.A.) covering the period from 1877 to 1957, and contains a directory giving details of differential thermal analysis equipment, the names of the users, and notes of the applications in various laboratories throughout the world.

The text, which occupies only about one third of the work, opens with an historical introduction and goes on in Chapter 1 to describe the development of early forms of D.T.A. apparatus used in the study of clays and in metallurgy. Chapter 2 deals fully with the various items of equipment under the headings of: sample holders, thermocouples, furnaces, rate controllers and recorders; and ends with a description of the special equipments which have been used for high temperature work and for work in controlled atmospheres including vacuum. Also included is a reprint of the A.S.T.M.'s specification E14-51T. Next, there follows a discussion of the factors involved in the qualitative use of the technique and this is illustrated in Chapter 4 by a description of some selected applications of it to the analysis of mixtures, phase studies, the sorption of ions and the transformation of clays. This section concludes with a consideration of the use of other qualitative techniques such as X-ray and chemical analysis, dilatometry, microscopy and weight loss, which may be used to assist in the interpretation of D.T.A. results. Quantitative aspects are introduced in Chapter 5 (by N. F. Tsang) which deals with the various mathematical treatments which have been applied to account for the form of the D.T.A. curve. The simple theories of Speil and Vold are described first, followed by an account of conduction theory and the equivalent system, the latter being illustrated by some numerical examples. Chapter 6 then goes on to consider the methods used by various workers to obtain quantitative data from experimental D.T.A. records. Finally, some further applications of the technique in the study of radiation damage and in geology, chemistry and ceramics are outlined, and the text closes with a chapter on more recent developments and applications.

In view of the large number of references which are given it is not surprising that little attempt has been made by the authors to provide a critical appraisal of the published work. It is without doubt the most compendious reference work on this subject which has appeared to date, and should prove invaluable to most workers in D.T.A. The appendices on the operators of D.T.A. equipment are most useful and, very important in a review of this kind, the applications of D.T.A. to specific substances are indexed with their appropriate literature references.

For the most part the book is well written, although the small size of type used for the subscripts in the mathematical sections occasionally leads to difficulties, and some typographical errors of punctuation make a few sentences read a little strangely. These, however, are minor defects and the authors are to be congratulated on the successful presentation of a very large quantity of data. Whilst the book sets out to review the applications of D.T.A. in the whole field of chemistry and chemical technology, it is clear that by far the greater proportion of work using the technique has so far been concentrated in mineralogy and in ceramics. Nevertheless, the book makes it equally clear that the method has wide scope and it is to be hoped that the authors' efforts will stimulate increased effort in those areas where hitherto it has received little attention.

C. P. CONDUIT

NOTICES

The following meetings have been arranged:

Tuesday 25 *November* 1958: **Society for Analytical Chemistry,** Physical Methods Group: Annual General Meeting followed by a meeting on *Modern Methods of Purification*: *Preparative Scale Gas Chromatography*: Dr. C. R. PATRICK, A.R.I.C. *Some Aspects of the practice of Zone Refining*: Dr. C. R. VEALE, A.R.I.C. Chemical Society Meeting Room, Burlington House, London, W.1. 6.30 p.m.

Thursday 27 *November* 1958: **Chemical Society,** Northern Ireland Area: **Royal Institute of Chemistry,** Northern Ireland Section: **Society of Chemical Industry,** Northern Ireland Section. *Analytical Applications of Co-ordination Compounds:* Dr. T. S. WEST. The Queen's University, Belfast. 7.45 p.m.

Thursday 27 *November* 1958: **Chemical Society,** Sheffield Area, **Royal Institute of Chemistry,** Sheffield, South Yorkshire and North Midlands Section: **Sheffield University Chemical Society.** *Organic Complexing Agents in Analytical Chemistry*: Dr. H. M. N. H. IRVING, F.R.I.C., Chemistry Department, The University, Sheffield. 7.30 p.m.

Wednesday 3 *December* 1958: **Society for Analytical Chemistry.** *Food Analysis*: Symposium. The Wellcome Building, Euston Road, London, N.W.1. 3.0 p.m.

Thursday 4 *December* 1958: **Society for Analytical Chemistry,** North of England Section: **Royal Institute of Chemistry,** North Lancashire Section. *Some Recent Advances in Polarography and Other Electrical Methods:* G. F. REYNOLDS, M.Sc., F.R.I.C. Storey Institute, Lancaster. 7.30 p.m.

Tuesday 9 *December* 1958: **Society for Analytical Chemistry,** Midlands Section. *The Analysis of Tar Acids:* H. G. WILLCOCK. Gas Showrooms, Nottingham. 7.0 p.m.

Tuesday 9 *December* 1958: **Society for Analytical Chemistry,** Biological Methods Group. Annual General Meeting followed by a Discussion Meeting. "The Feathers", Tudor Street, London, E.C.4. 6.30 p.m.

Wednesday 10 *December* 1958: **Society for Analytical Chemistry,** Microchemistry Group: London Discussion Meeting. "The Feathers", Tudor Street, London, E.C.4. 6.30 p.m.

Wednesday 17 *December* 1958: **Society for Analytical Chemistry,** Midlands Section. Discussion on *Flame Photometry*, to be opened by L. BREALEY, B.Sc. The University, Edgbaston, Birmingham 15.

Friday 19 *December* 1958: **Society for Analytical Chemistry,** Western Section: **Royal Institute of Chemistry,** Cardiff and District Section. *New Techniques in Qualitative Analysis:* D. W. WILSON, M.Sc., F.R.I.C. Cardiff.

Wednesday 7 *January* 1959: **Royal Institute of Chemistry,** Bristol and District Section. Christmas Lecture: *Chromatography:* Dr. F. H. POLLARD. Royal Fort, Bristol, 8.

Tuesday 13 *January* 1959: **Society for Analytical Chemistry,** Midlands Section. Discussion on *The Analytical Chemistry of Cobalt and Nickel*, to be opened by A. J. BROOKES. The University, Edgbaston, Birmingham 15.

Hilger Journal, Vol. V, No. 1 for August 1958 (Hilger and Watts, Ltd., 98 St. Pancras Way, Camden Road, London, N.W.1., England) contains articles dealing with automatic typewriter attachments for recording of spectrographic results, with statistical procedure in relation to spectrochemical analysis, and with atomic-absorpion spectroscopy using the UVISPEK spectrophotometer.

A Bibliography has been prepared (Development Division, the Geigy Company Ltd., Rhodes, Middleton, Manchester, England) dealing with the analytical uses of ethylenediaminetetra-acetic acid. The nine sections of the Bibliography contain more than a thousand references, and a comprehensive subject index is provided.

The earliest ten volumes of *The Analyst*, for the years 1876–1885, have been re-published in facsimile form by W. Heffer & Sons Ltd., of Cambridge, who are currently publishers of that journal on behalf of **The Society for Analytical Chemistry.** Each volume is available separately from any bookseller or direct from the publishers at 6 gns. nett, bound in cloth boards in the style of the original. Publication in America is through the Johnson Reprint Corporation.

Talanta, 1958, Vol. 1, p. 415. Pergamon Press Ltd., London.

BOOK RECEIVED

Advanced Analytical Chemistry. LOUIS MEITES and HENRY C. THOMAS. McGraw-Hill Book Company Inc., New York: McGraw-Hill Publishing Company, Ltd., London, 1958. pp. xi + 540. $8.90. 69s.

PAPERS RECEIVED

Ferrous Iron-Sulphuric Acid Reagent for the Determination of Pure Oestrogens. EMMANUEL EPSTEIN WILLIAM O. MADDOCK and A. J. BOYLE. (26 *August* 1958.)

Photometric Determination of Gallium Using Malachite Green. J. JANKOVSKY. (17 *September* 1958.)

Direct Thermometric Titration of Boric Acid. F. J. MILLER and P. F. THOMASON. (19 *September* 1958.)

Studies on Materials Containing Uronic Acid—I: An Apparatus for Routine Semi-Micro Determinations of Uronic Acid Content: D. M. W. ANDERSON. (17 *September* 1958.)

The Determination of Aluminium, Titanium and Nickel in Their Alloys. LOUIS E. HIBBS and DONALD H. WILKINS. (22 *September* 1958.)

The Determination of Aluminium in Thorium Oxide, and a Separation Scheme for Interfering Ions. GERALD GOLDSTEIN, D. L. MANNING and OSCAR MENIS. (22 *September* 1958.)

Visual EGTA Titration of Calcium in the Presence of Magnesium. FAWZY S. SADEK, R. W. SCHMID and CHARLES N. REILLEY. (27 *September* 1958.)

Titrimetric Determination of Manganese following Nitric Acid Oxidation in the Presence of Pyrophosphate. C. OLIVER INGAMELLS. (3 *October* 1958).

The Determination of Copper with Triethylenetetramine using a Metalfluorechromic Indicator. DONALD H. WILKINS and LOUIS E. HIBBS. (3 *October* 1958).

Activation Analysis of Tungsten in High Alloy Steels. G. LELIAERT, J. HOSTE and Z. EECKHAUT (6 *October* 1958.)

Titrimetric Determination of Tetraphenylboron by Thallium^{I}. BHARAT R. SANT and ANIL K. MUKHERJI. (13 *October* 1958).

New Chelons Based on Pyridine. DAVE C. PRIEST, FAWZY S. SADEK, J. F. BUNNETT and CHARLES N. REILLEY. (20 *October* 1958).

Determination of Protactinium-233 by Gamma Spectroscopy. E. I. WYATT and R. R. RICKARD. (22 *October* 1958).

The Use of EDTA to Eliminate Interference in the Zinc-Ferrocyanide Titration. DONALD G. DAVIS and HENRY T. MCLENDON. (23 *October* 1958).

A New Spot Test for the Determination of Fluoride Ion. R. BELCHER, M. A. LEONARD and T. S. WEST. (29 *October* 1958).

EDITORIAL NOTE

The editors and publishers are grateful for the patience of those authors who submitted material when *Talanta* was first projected, and who, because of the large number of papers submitted, have had to await publication until this issue.

It is hoped normally to offer the following schedule: short communications and preliminary communications (particularly if they do not involve illustrations) should be published within 30 to 60 days, and longer communications within 3 to 4 months of acceptance for publication.

Single issues of *Talanta* will normally consist of approximately 80 pages, and the Volume as a whole will contain 4 issues. The next issue, which will be Number 1 of Volume 2, is planned for publication in two months' time.

Talanta, 1958, Vol. 1, p. 416, Pergamon Press Ltd., London.

ERRATA

Page 121, *line* 17: *for* M^{2-} *read* M^{2+}

Page 122, *Fig.* 4 (*upper graph*): *for* 255 mμ *read* 225 mμ. *Transpose Curves* 1 *and* 2.

Page 123, *Fig.* 6. *Replace legend by the following:*

(1) 10 μM magnesium chloride + reagent blank; (2) 10 μM calcium chloride + 1 μM magnesium chloride + reagent blank; (3) 10 μM strontium chloride + 1 μM magnesium chloride + reagent blank; (4) 10 μM barium chloride + 1 μM magnesium chloride + reagent blank.

Page 124, *Table* III. *Error column should read as follows:*

Cation	Error (μM)	Cation	Error (μM)
Magnesium	−0·20 0 +0.04 −0·15	Strontium	−0·14 +0·02 0 +0·07
Calcium	−0·05 +0·20 −0·20 −0·02	Barium	+0·10 +0·14 +0·08 +0·09

Page 126. *Ref.* 16 *should read: Analyst.* 1956, **81,** 79.

Page 180. *Replace existing Fig.* 4 *by*

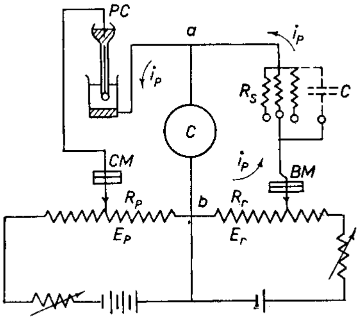

FIG. 4. Compensating bridge circuit.

TALANTA

An International Journal of Analytical Chemistry

VOLUME 1 1958

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AUTHOR INDEX

(*Names of authors of books reviewed are in italics*)

Progress in Nuclear Energy
The International Review Series in
Atomic Energy

Editorial Advisory Group:
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EDITED PROCEEDINGS OF THE SECOND INTERNATIONAL CONFERENCE ON THE PEACEFUL USES OF ATOMIC ENERGY, GENEVA

SEPTEMBER 1958

PERGAMON PRESS is pleased to announce that the Board of Editors of Progress in Nuclear Energy, the International Review Series in Atomic Energy, have made arrangements to publish the Edited Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy in twelve separate volumes, similar to those edited by them and published by Pergamon Press on the First International Conference on the Peaceful Uses of Atomic Energy held in Geneva in 1955.

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Process Chemistry	III	F. R. Bruce, Oak Ridge. J. M. Fletcher, Harwell. H. H. Hyman, Argonne.
Technology and Engineering	IV	R. Hurst, Dounreay. R. N. Lyon, Oak Ridge.
Metallurgy and Fuels	V	H. M. Finniston, Harwell. J. P. Howe, Canoga Park, California.
Biological Sciences	VI	J. Bugher, Rockefeller Foundation. J. Coursaget, Saclay. J. F. Loutit, MRC Harwell.
Medical Sciences	VII	J. Bugher, Rockefeller Foundation. J. Coursaget, Saclay. J. F. Loutit, MRC Harwell.
Economics of Nuclear Power	VIII	J. A. Lane, Oak Ridge. Philip Sporn, New York. P. W. Mummery, Harwell. I. R. Maxwell, London.
Analytical Chemistry	IX	Editors being appointed.
Law and Administration	X	Herbert S. Marks, Washington, D.C.
Plasma Physics and Thermo-Nuclear Research	XI	J. L. Tuck, Los Alamos. C. Longmire, Los Alamos. W. B. Thompson, Harwell.
Health Physics	XII	Karl Z. Morgan, Oak Ridge. W. G. Marley, Harwell.

Some of the Topics to be covered in these Edited Proceedings:
The Future of Nuclear Power. Experience with Nuclear Power Plants. The Use of Nuclear Energy for purposes other than the generation of electricity (for example, Marine Propulsion). The possibility of developing Thermonuclear Power (by fusion instead of fission). Progress in the use of Radioactive Isotopes. Operational Aspects in Health and Safety. Aspects in Nuclear Power Programmes. Recent Developments in Fundamental Physics. Reactor Technology and Chemistry. Properties of Reactor Materials. Treatment and Handling of Radioactive Wastes. Processing of Irradiated Fuel Elements. Problems in Nuclear Fusion. Fuel Cycles and Economics of Nuclear Power. Use of Research and Test Reactors and Reactor Experiments. Dosimetry and Standards. New Uses of Isotopes in Medicine. Use of Isotopes in Biochemistry and Physiology. Use of Isotopes in Research, Control and Industrial Technology. Use of Isotopes in Agriculture. Experience in Radiological Protection. Biological Effects of Radiation. Fabrication of Fuel Elements including the Metallurgy of Uranium, Thorium, Plutonium and their Alloys.

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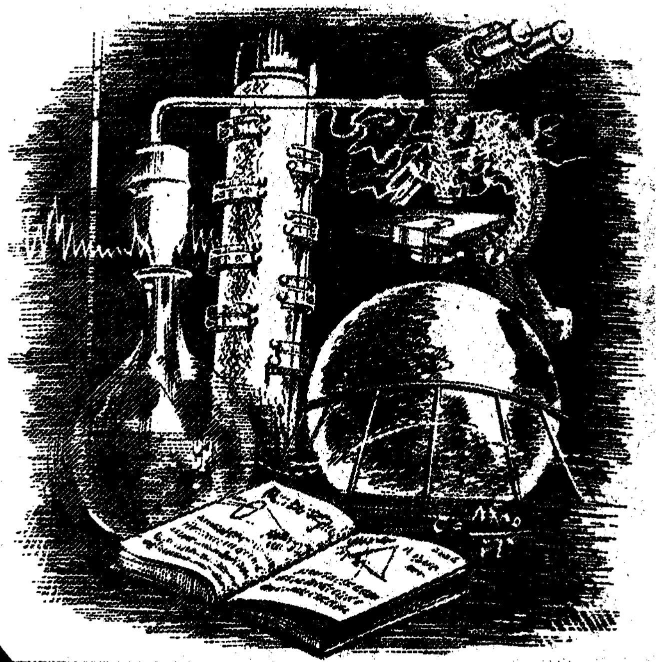

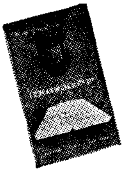

NOTES FOR CONTRIBUTORS

1. General

Contributions may deal with any aspect of analytical chemistry, although papers exclusively concerned with limited fields already catered for by specialist journals should normally be directed to those journals, and should only be submitted to TALANTA if their analytical implications as a whole are such as to make their inclusion in a more general background desirable.

Original papers, short communications, preliminary communications and reviews will be published. Suitable books submitted to the Editor-in-Chief will be reviewed.

Since TALANTA is an international journal, contributions are expected to be of a very high standard. Research papers should make a definite contribution to the subject. Special importance will be attached to work dealing with the principles of analytical chemistry in which the experimental material is critically evaluated, and to similar fundamental studies. Reviews in rapidly expanding fields, and reviews of hitherto widely scattered material, will be considered for publication, and should be critical. The Editor will welcome correspondence on matters of interest to analytical chemists.

All papers and short communications submitted for consideration will be refereed in the normal way. Referees will be encouraged to present critical and unbiassed reports which are designed to assist the author in presenting his material in the clearest and most unequivocal way possible. To assist in achieving this completely objective approach, referees will be asked to submit signed reports. At the discretion of the Editor the names of referees may be disclosed if thereby agreement between author and referee is likely to result. Authors should appreciate that the comments of referees are presented in a constructive spirit, and that agreement between the views of author and referee must result in a higher standard of publication.

It is hoped that research and review papers will be published within approximately three to four months of acceptance, and short communications within two months.

Twenty-five free reprints of each paper will be provided (with ten further free copies for each additional author) and additional copies can be supplied at reasonable cost if ordered when proofs are returned. A reprint order form will accompany the proofs.

2. Script Requirement

1. Contributions should be submitted to the Editor-in-Chief, or to the appropriate Regional Editor, and may be written in English, German or French.

2. Scripts should be submitted in duplicate. They must be typewritten and the lines double-spaced. Where possible, research papers should follow the pattern: *Introduction*, *Discussion*, *Conclusion*, *Experimental* (or such of these headings as apply.)

3. Summaries will not be required for short or preliminary communications. For other contributions the essential contents of each paper should be briefly recapitulated in a summary at the beginning of the paper. This should be in the language of the paper, but for German or French papers an English version should also be provided wherever possible. Summaries of papers will be printed in all three languages, and authors who are able to provide translations of their summaries are asked to do so.

4. Illustrations should be separate from the typescript of the paper and legends should also be typed on a separate sheet. Line drawings which require redrawing should include all relevant details and clear instructions for the draughtsman. If figures are already well drawn, it may be possible to reproduce them direct from the originals, or from good photoprints, if these can be provided; it is not possible to reproduce from prints with weak lines. Illustrations for reproduction should normally be about twice the final size required. The following standard symbols should be used on line drawings, since they are easily available to the printers:

△ △ ⊡ □ ● ○ ◬ ⊙ ⊕ ⊖ ⏻ ⊗

5. Tables should if possible be so constructed as to be intelligible without reference to the text, every table and column being provided with a heading. Units of measure must always be clearly indicated. Unless it is essential to the argument, tables should not list the results of individual experiments, but should summarise results by an accepted of method expression, *e.g.*, standard deviation. The same information should not be reproduced in both tables and figures.

6. References should be indicated in the text by consecutive superior numbers; and the full reference, including title of paper where desired, should be given in a list at the end of the paper in the following form:

[1] J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.
[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds*. Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.
[3] A. B. Smith, *The Effect of Radiation on Strengths of Metals*. A.E.R.E., M/R 6329, 1962.
[4] W. Jones, *Brit. Pat.* 654321, 1959.

Footnotes, as distinct from literature references, should be indicated by the following symbols: *, †, ‡, ¶, commencing anew on each page; they should not be included in the numbered reference system.

7. Except in the case of preliminary communications, proofs will be sent to authors for correction when their contribution is first set, but there is rarely time for page proofs also to be sent for checking. This will be done, however, when the amount of alteration makes it advisable.

8. Because of the international character of the Journal, no rigid rules concerning spelling, notation or abbreviation need be observed by authors, but each paper or series of papers should be self-consistent as to symbols and units.

NOVEMBER 1958 VOLUME 1 NUMBER 4

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Preliminary Communications:

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